APPENDIX B
GENERATOR EXPERIMENTS AND DATA

The study of the sampling and analysis procedures of the Semi-VOST method was divided into two parts: sample generation studies presented here and laboratory analytical studies which are presented in Appendix D.

OBJECTIVE

The objective of the sample generation studies was to determine the effect of sampling conditions and flue gas composition on the amount of hydrocarbons recovered from the sampling train. Variables which were considered to potentially affect method performance included:

- moisture,
- sulfur dioxide,
- hydrochloric acid,
- oxides of nitrogen,
- sample volume,
- sampling flow rate, and
- hydrocarbon or POHC concentration.

APPROACH

The first task in this study was to select a set of test compounds which would be representative of principal organic hazardous constituents (POHCs). The criteria for compound selection included: (1) incinerability, (2) solubility in water, (3) boiling point, and (4) chemical functionality.

With these criteria in mind, a series of 12 compounds was selected for study which included a range of boiling points from 102°C (1,4-dioxane) to 310°C (pentachlorophenol). Initial experiments were conducted to determine the minimum detection limit (MDL) for each of the 12 compounds

combined into a single solution. The analyses were performed using GC/MS. The MDL values and boiling points for these compounds are presented in Table B-1.

A flue gas simulator was then designed and constructed to evaluate the performance of the method in the laboratory. The simulator, illustrated in Figure B-1, was sized to deliver sufficient "stack" gas volume flows to be sampled simultaneously by two Semi-VOST trains through a heated glass manifold. A hydrocarbon-free air sample stream of approximately 0.6 dscm/min was provided by pumping ambient air through a high temperature catalytic oxidizer and a Perma-Pure® polymeric drier. The air stream was then split with half of the total flow heated to approximately 250°C before introduction of POHCs. Solutions of the test compounds were prepared in methanol and introduced into the hot air stream through a 5-mL motor-driven syringe. Typical solution delivery rates ranged between 20-30 µL/min. The air containing POHCs was then re-heated through a glass mixing bulb before introduction of water, HCl, SO_2, NO_x, and the other half of the clean air stream. Sulfur dioxide and NO_x were introduced from cylinder gas mixtures. HCl was introduced by acidifying the water being metered into the air mixture. The "stack" gas then passed through a second, heated, mixing bulb before entering a glass sampling manifold heated to approximately 300°C. The design parameters provided for 20 percent maximum flue gas moisture levels.

Table B-2 presents a listing of sample generation variables addressed in the study. Table B-3 outlines the test matrix conditions which were based upon a one-half replicate of a 2^5 factorial experimental design. The operating conditions are listed in terms of (1), ab, cd, ae, abcd, etc., as given in the design. The symbol "1" represents Level I of all five independent operating variables. Symbol "ab" represented Level II of Variable A and Variable B, and Level I for Variables C, D, and E.

The draft method formulation was initially followed for both the sampling and analysis of the recovered samples. However, the train rinsing procedure and subsequent sample work-up procedure were modified as now presented in Appendix A.

TABLE B-1. MINIMUM DETECTION LIMIT (MDL)
FOR GC/MS ANALYSIS OF TEST COMPOUNDS OF METHANOL

Selection criteria	Test compound	Boiling point, °C	MDL ng/uL
Incinerability	1,1,2,2-Tetrachloroethane	146	0.25
	Pentachlorophenol	310	4.2
	Hexachloroethane	(sublimes)	0.90
Water solubility	Urethane	180	10.1
	Pyridine	115	8.5
	1,4-Dioxane	102	7.0
Boiling point	Naphthalene	218	0.32
	Chlorobenzene	132	0.37
	Toluene	110	1.9
Chemical functionality	Phenol	182	5.0
	Nitrobenzene	211	1.1
	Resorcinol	280	7.3

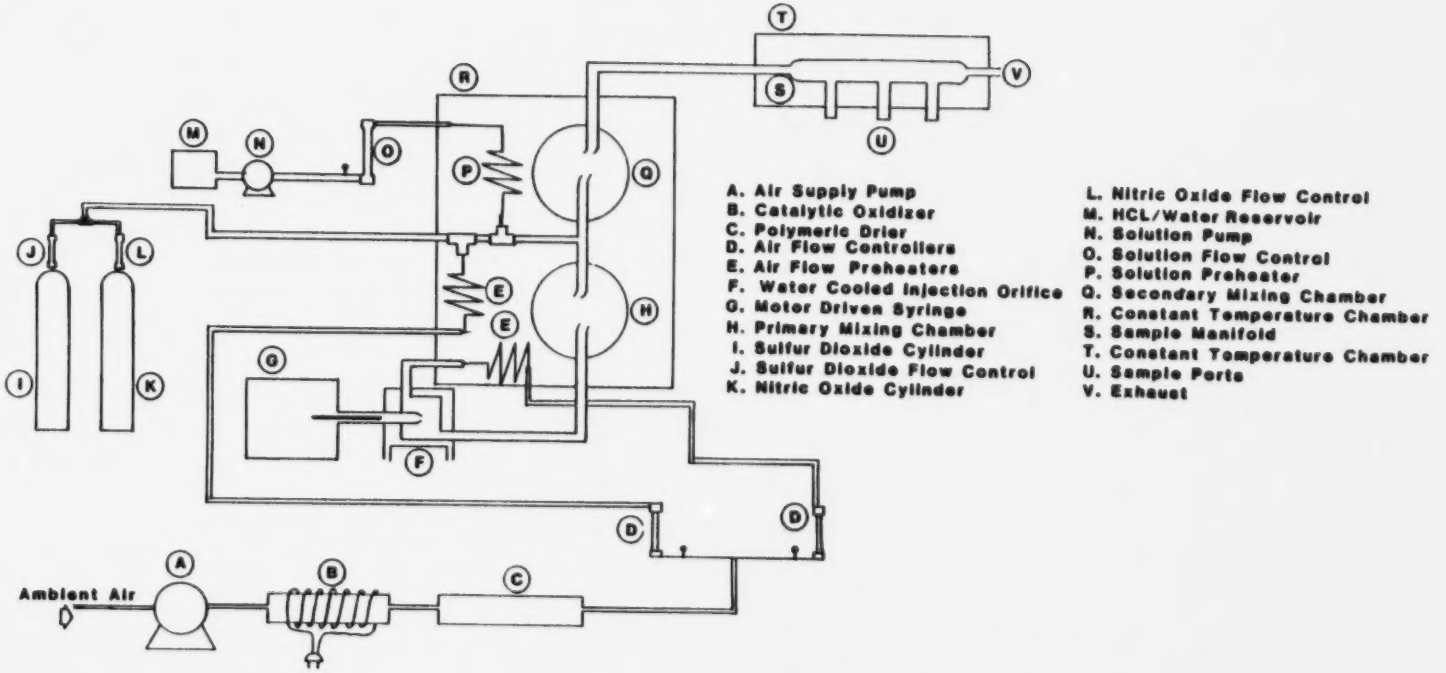


Figure B-1. Flue gas simulation system.

TABLE B-2. SAMPLE GENERATION VARIABLES

Variable	Level I	Level II
A	Low moisture High SO_2 (~750 ppmv) High HCl (~1,000 ppmv)	High moisture Low SO_2 (~50 ppmv) Low HCl (~50 ppmv)
B	Low NO_x (~250 ppmv)	High NO_x (~1,000 ppmv)
C	Low hydrocarbon concentration (~3 MDL)	High hydrocarbon concentration (~10 MDL)
D	Small sample size (~0.6 m^3)	Large sample size (~14 m^3)
E	Low sample flow rate (~0.0028 dscm/min)	High sample flow rate (~0.021 dscm/min)

TABLE B-3. OPERATING LEVELS FOR A 1/2 REPLICATE OF A 2^5 FACTORIAL EXPERIMENT*,†

Block 1	Block 2
(1)	ac
ab	bc
cd	ad
ae	bd
be	ce
abcd	de
acde	abce
bcde	abde

* Reference. Cochran, William G. and Gertrude M. Cox, "Expeimental Designs" Second Edition, John Wiley and Sons, Inc., New York, 1957.

† Block 1 experimental conditions were run on one Semi-VOST train and Block 2 conditions were run on a second Semi-VOST train.

With the proposed design it was possible to determine all the main effects, A, B, C, D, and E, and the two-factor interaction terms, AB, BC, CD, etc. The latter gave some indication of the independence of the main factors. The response (dependent) variable in each case was the amount of hydrocarbon extracted from the XAD-2® resin.

The proposed design given in Table B-3 confounds the CD interaction (which is also the ABE interaction) with Blocks 1 and 2. This design was selected so that the sets of runs indicated for each block could be run on two separate sample trains. It was assumed a priori that the CD interaction should be negligible because of the nature of Variables C and D. Doubling the inlet composition of the material entering the bed should double the amount recovered from the bed. Doubling the sample size should also double the amount recovered from the bed. Doubling both the composition and the sample size should quadruple the amount recovered from the bed. This assumption also implies that the XAD-2® resin bed is not saturated with hydrocarbon, i.e., there is no breakthrough.

RESULTS

A summary of the results for the flue gas generator studies is given in Table B-4 in which the data are expressed as percent recovery. Runs 1 and 2 were initial experiments in which only the test compounds were added at the 10 MDL level to a clean air stream and sampled by two Semi-VOST trains "A" and "B." These tests were used to provide an indication of the baseline error for the analysis of subsequent results. The remainder of the tests were carried out by collecting samples with a single train over the range of test conditions. Table B-5 gives the distribution of each compound within a given train as a percentage of the total amount recovered.

TABLE B-4. GENERATOR STUDY, SUMMARY PERCENTAGE RECOVERIES

	Run 1		Run 2		Operating conditions															
	A	B	A	B	(1)	ab	cd	ae	be	abcd	acde	bcde	ac	bc	ad	bd	ce	de	abce	abde
Dioxane	105	83	71	103	100	78	104	112	87	89	133	87	115	67	111	105	114	109	115	101
Pyridine	51	41	31	63	10	41	73	61	14	56	105	88	103	9	69	52	156	27	35	91
Toluene	80	68	82	95	84	84	72	86	75	74	161	93	68	73	117	119	71	141	75	112
Urethane	65	61	74	121*	81	40	48	60	15	32	65	67	67	4	58	38	99	26	59	33
Chlorobenzene	87	71	79	101	90	94	98	107	82	97	123	101	88	85	109	113	93	93	95	110
1,1,2,2-tetra-chloroethane	95	71	84	94	98	105	109	109	86	100	141	113	98	87	99	117	105	104	99	121
Phenol	79	99	77	93	100	71	81	108	66	66	113	105	92	77	81	77	111	86	94	64
Nitrobenzene	85	79	82	101	100	110	107	119	97	106	116	116	108	98	110	131	112	119	110	121
Hexachloroethane	84	80	83	91	100	99	99	117	93	104	104	115	98	101	92	107	101	112	112	102
Naphthalene	92	91	90	99	110	95	100	112	102	100	119	119	95	110	91	110	97	135	101	111
Resorcinol	0	0	0	0	0	0	0	0	23	0	0	1	11	0	0	0	10	0	0	0
Pentachlorophenol	0	0	0	0	0	83	226	169	77	177	0	201	136	22.5	121	120	182	633	219	0

* Suspected outlier.

TABLE B-5. DISTRIBUTION OF COMPOUNDS WITHIN THE SAMPLING TRAIN, PERCENT OF TOTAL COLLECTED

	Dioxane	Pyridine	Toluene	Urethane	Chloro-benzene	1,1,2,2-tetra-chloroethane	Phenol	Nitro-benzene	Hexachloro-ethane	Naphtha-lene	Resorcinol	Pentachloro-phenol
Run 1 Train A												
Rinse	5.9	10.3	.6	ND*	<.1	<.1	2.0	ND	ND	1.0	ND	ND
Condensate	NO SAMPLE*										NO SAMPLE	
XAD	94	89.6	98	100	99.8	99.9	97.9	100	100	99	ND	ND
Impinger	ND	<.1	1.1	ND	<.1	ND	ND	ND	ND	ND	ND	ND
Run 1 Train B												
Rinse	ND	25.6	ND	ND	ND	ND	4.8	0.1	ND	ND	ND	ND
Condensate	NO SAMPLE										NO SAMPLE	
XAD	100	74.4	99.7	100	99.9	100	95.3	99.9	100	99.7	100	ND
Impinger	ND	ND	0.3	ND	.1	ND	ND	ND	ND	.3	ND	ND
Run 2 Train A												
Rinse	ND	ND	ND	ND	ND	.2	.2	ND	ND	27.1	ND	ND
Condensate	NO SAMPLE										NO SAMPLE	
XAD	100	100	99.1	100	99.9	99.8	99.8	100	100	73	ND	ND
Impinger	ND	ND	.9	ND	.1	ND	ND	ND	ND	ND	ND	ND
Run 2 Train B												
Rinse	5.8	8.3	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
Condensate	NO SAMPLE										NO SAMPLE	
XAD	94.2	91.7	100	100	99.9	100	100	100	100	100	ND	ND
Impinger	ND	ND	ND	ND	<.1	ND	ND	ND	ND	ND	ND	
bc Train A												
Rinse	8.2	4	10.9	ND	ND	1.1	58	2.6	ND	3	ND	90.2
Condensate	NO SAMPLE										NO SAMPLE	
XAD	89.6	96	89	100	100	98.9	42	97.4	100	97	ND	9.9
Impinger	2.4	ND	.1	ND	ND	ND	ND	ND	ND	ND	ND	ND
be Train B												
Rinse		75.6	ND	61	.8	2.6	26.2	11	3.5	17.4	100	ND
Condensate	NO SAMPLE										NO SAMPLE	
XAD	79.9	22.4	99.7	39	99.2	97	38.7	89	96.5	82.6	ND	100
Impinger	20	2.1	.3	ND	ND	.3	35.1	ND	ND	ND	ND	ND

(continued)

Table B-5. (continued)

	Dioxane	Pyridine	Toluene	Urethane	Chloro-benzene	1,1,2,2-tetra-chloroethane	Phenol	Nitro-benzene	Hexachloro-ethane	Naphtha-lene	Resorcinol	Pentachloro-phenol
de Train A												
Rinse	ND	ND	13	ND	ND	ND	ND	.4	.3	7.6	ND	ND
Condensate	19.7	92.4	.1	100	ND	1.4	68.4	ND	ND	ND	ND	ND
XAD	76.9	7.6	86.5	ND	100	98.6	31.5	99.6	99.7	92.5	ND	100
Impinger	3.5	ND	.3	ND	ND	ND	ND	ND	ND	ND	ND	ND
(1) Train B												
Rinse	ND	94	ND	ND	ND	2	ND	ND	ND	4.3	ND	ND
Condensate	NO SAMPLE										NO SAMPLE	
XAD	100	6	99.7	100	100	98	100	100	100	95.7	ND	ND
Impinger	ND	ND	.3	ND	ND	ND	ND	ND	ND	ND	ND	ND
ac Train A												
Rinse	4.6	16.9	.5	11	ND	ND	7.4	.3	ND	<.1	ND	29
Condensate	NO SAMPLE										NO SAMPLE	
XAD	80.5	32.7	96.6	32.9	99.8	99	56.9	99.1	100	98.9	100	69.8
Impinger	15.1	50.4	.8	56.1	.2	1	35.8	.2	ND	<.1	ND	.9
acde Train B												
Rinse	6.2	<.1	.4	.6	ND	.3	.5	<.1	ND	ND	ND	ND
Condensate	35.5	87.6	.2	90	ND	ND	74.8	1.4	ND	<.1	ND	ND
XAD	47.1	ND	99.1	ND	99.9	99.7	14.3	98.6	100	99.9	ND	
Impinger	11.2	12.2	.3	9.5	<.1	ND	10.5	ND	ND	ND	ND	ND
ab Train B												
Rinse	4.8	20.5	.6	4.2	ND	ND	4.3	.2	ND	<.1	ND	16.9
Condensate	NO SAMPLE										NO SAMPLE	
XAD	81.1	10.8	98.4	30.4	99.5	97.2	75.5	99.6	100	99.7	ND	83.1
Impinger	14.1	68.7	.9	65.5	.5	2.8	20.2	.3	ND	.2	ND	ND
ad Train A												
Rinse	NA†	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA
Condensate	41.3	94	.3	86.2	ND	ND	24.1	ND	ND	ND	ND	ND
XAD	44.2	4.8	99.5	12.9	100	100	75.9	100	100	100	ND	100
Impinger	14.6	1.1	.1	.8	ND	ND	ND	ND	ND	ND	ND	ND

(continued)

Table B-5. (continued)

	Dioxane	Pyridine	Toluene	Urethane	Chloro-benzene	1,1,2,2-tetra-chloroethane	Phenol	Nitro-benzene	Hexachloro-ethane	Naphtha-lene	Resorcinol	Pentachloro-phenol
bcde Train A												
Rinse	.8	<.1	1.7	.5	.3	.2	.8	.2	.3	.5	5.3	65.7
Condensate	46	99.1	<.1	96.1	<.1	.1	81.7	2.5	ND	<.1	44.5	2.5
XAD	49.5	.7	98.3	3.3	99.6	99.7	.2	97.2	99.7	99.5	50.2	31.8
Impinger	3.8	.2	<.1	.2	<.1	<.1	.2	<.1	<.1	<.1	ND	<.1
ae Train B												
Rinse	4.4	31.4	.9	6.2	<.1	ND	3.2	.5	ND	.2	ND	44.2
Condensate	NO SAMPLE										NO	SAMPLE
XAD	33.1	5.6	98.5	7.7	99.8	99.5	15	96.4	100	99.7	ND	55.8
Impinger	62.5	63	.5	86.1	.2	.5	81.8	3.1	ND	.1	ND	ND
abce Train A												
Rinse	7.4	36	.5	5.7	ND	1.4	3.3	.4	ND	<.1	ND	42.3
Condensate	NO SAMPLE										NO	SAMPLE
XAD	31.1	1.8	98.3	4.6	99	96.3	11.3	90.1	99.9	99.7	ND	54.4
Impinger	61.5	62.2	1.3	89.8	.6	2.3	85.2	10.1	<.1	.3	ND	3.4
ce Train A												
Rinse	7.8	5.3	.6	3.2	<.1	ND	2.2	.2	ND	<.1	8.5	48.2
Condensate	NO SAMPLE										NO	SAMPLE
XAD	56.5	7.3	98.8	35.7	99.9	98.8	79	99.8	100	99.9	91.5	51.7
Impinger	35.7	87.6	.5	61.1	.1	1.2	19.1	<1	ND	<.1	ND	ND
bd Train A												
Rinse	3.5	11.2	.7	66.5	ND	ND	1.4	ND	ND	ND	ND	ND
Condensate	16.2	56	.2	28.5	ND	ND	15.2	ND	ND	ND	ND	ND
XAD	71.1	21.1	98.7	3.3	99.8	99.7	82.4	100	100	99.9	ND	100
Impinger	9.2	11.5	.5	1.6	.2	.3	.9	ND	ND	<.1	ND	ND
abcd Train B												
Rinse	2.4	11.7	.4	ND	<.1	.4	.2	<.1	ND	<.1	ND	ND
Condensate	22.6	78.5	.2	80	ND	.2	17.8	.2	ND	<.1	ND	ND
XAD	67.4	9.2	98.8	20	99.9	99.2	82	99.8	100	99.9	ND	100
Impinger	9.1	.7	.6	ND	<.1	.2	ND	<.1	ND	<.1	ND	ND

(continued)

Table B-5. (continued)

	Dioxane	Pyridine	Toluene	Urethane	Chloro-benzene	1,1,2,2-tetra-chloroethane	Phenol	Nitro-benzene	Hexachloro-ethane	Naphtha-lene	Resorcinol	Pentachloro-phenol
cd Train B												
Rinse	2.2	2.9	.7	ND	.1	<.1	1	<.1	ND	<.1	ND	6.7
Condensate	30	90.9	.1	92	ND	<.1	61.2	<.1	ND	ND	ND	ND
XAD	52.1	2.6	98.6	6.8	99.6	99.1	34.4	99.1	99.9	99.8	ND	93.4
Impinger	16	3.6	.6	1.3	.3	1.8	3.5	.4	.1	.3	ND	ND
abde Train A												
Rinse	9.8	.6	1.3	ND	.1	4.1	3.2	.5	ND	.2	ND	ND
Condensate	46	91.7	.5	92	ND	.2	79	2.1	ND	<.1	ND	ND
XAD	33.5	7.7	96.9	8	99.2	95	17.8	97.1	100	99.5	ND	ND
Impinger	11	ND	1.4	ND	.8	.7	ND	.3	ND	.3	ND	ND

* No water was collected.

APPENDIX C

SEMI-VOST METHOD INTERFERENCES/ARTIFACT FORMATION

INTRODUCTION

To investigate the possibility of formation of artifacts on XAD-2® resin or of the occurrence of artifacts from the decomposition of the XAD-2® resin or other processes, data developed during the laboratory generator studies (Appendix B) were examined for the occurrence of artifacts in the XAD-2® extracts. A computerized literature search was also performed in order to investigate any reports of the occurrence of artifacts in studies performed using XAD-2®.

EXAMINATION OF RADIAN-GENERATED DATA

Compounds which were spiked on XAD-2® resin for a study which involved variation in generator conditions included 1,4-dioxane, pyridine, toluene, urethane, chlorobenzene, 1,1,2,2-tetrachloroethane, phenol, nitrobenzene, hexachloroethane, naphthalene, resorcinol, and pentachlorophenol. Generator conditions which were varied included concentration of oxides of nitrogen, sample size, the concentration of sulfur dioxide, the concentration of HCl, moisture, hydrocarbon concentration, and sample flow rate. The original dataset was generated by GC/MS analysis in the full scan mode to determine compound recoveries under the various sets of generator conditions. However, to assess the possible formation of artifacts, eight sets of data generated by GC/MS analysis of XAD-2® extracts were examined for the presence of compounds other than spiked compounds, deuterated surrogate compounds, and the quantitation standard. The presence of any additional peaks might be attributed to the formation of artifacts.

Several solvent blanks were analyzed with the XAD-2® extracts and a chromatogram representative of the blanks is shown in Figure C-1. Compounds other than surrogate and quantitation standards which are

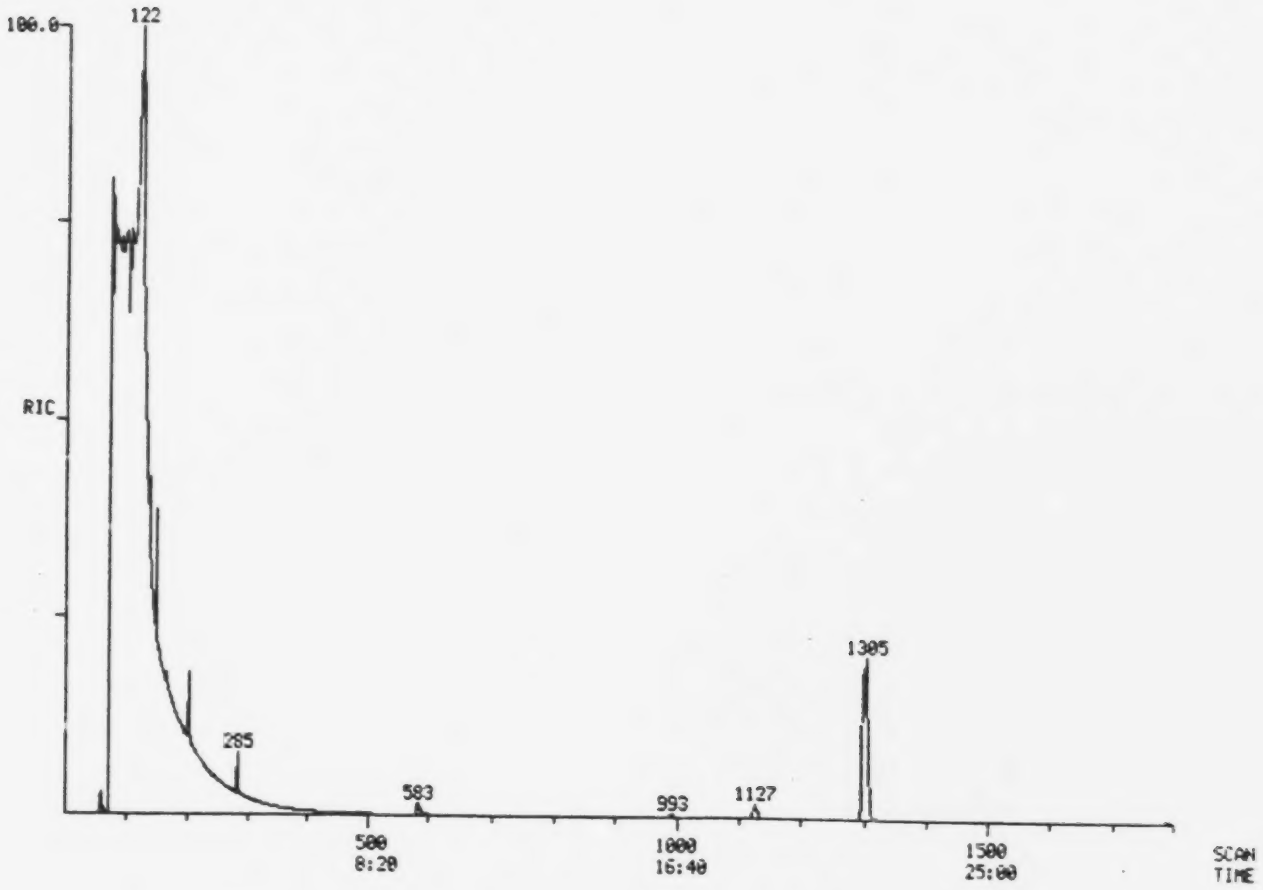


Figure C-1. Reconstructed gas chromatogram of a blank, with d_8-toluene (scan 203), carbon tetrachloride (scan 285), naphthalene (scan 583), dimethyl phthalate (scans 993 and 1127), and d_{10}-anthracene (scan 1305).

present in the blank can be attributed to a very low level of contamination. Figure C-2 shows a reconstructed gas chromatogram of a typical XAD-2® extract, and Table C-1 lists compounds which were typically identified in the XAD-2® extracts. These three analyses are typical of the 18 performed. The spiked compounds, deuterated surrogate compounds, and quantitation standard account for the majority of the peaks observed.

Of the remaining peaks, phthalate esters were identified which are plasticizers and are very often encountered as common solvent contaminants. Hexanol was observed in the blank and cannot thus be rationalized as coming exclusively from XAD-2® extracts. Volatile compounds such as chloroform, cyclohexane, and xylenes (always present at very low levels by comparison to the spiked compounds) are more readily explained as being contamination rather than by XAD-2® artifact formation due to their chemical structure. Fatty acid methyl esters are also frequently observed in the XAD-2® extracts at very low levels but it is difficult to rationalize an origin for these esters from decomposition of the resin or reaction of compounds with XAD-2® or spiked compounds. There is likewise no evidence such as the presence of substantial amounts of extraneous compounds to support the theory of possible formation of artifacts by interaction of the compounds with the extracting solvent.

The various generator conditions used to produce these samples do not seem to influence either type or quantity of artifact formation. The data clearly illustrate that formation of artifacts which can be extracted and analyzed by capillary gas chromatography/mass spectrometry does not appear to occur to any significant extent under the experimental conditions employed. Some of the compounds spiked, however, exhibit consistently poor recoveries. If these poor recoveries are due to formation of an artifact or occurrence of a chemical reaction, the resulting compound(s) may not be sufficiently volatile to be observed under the analytical conditions used.

SURVEY OF THE PUBLISHED LITERATURE

A computerized search of the available chemical literature yielded very little information pertinent to the question of artifact formation in the use/extraction of XAD-2®. Comparative evaluations of XAD-2® and

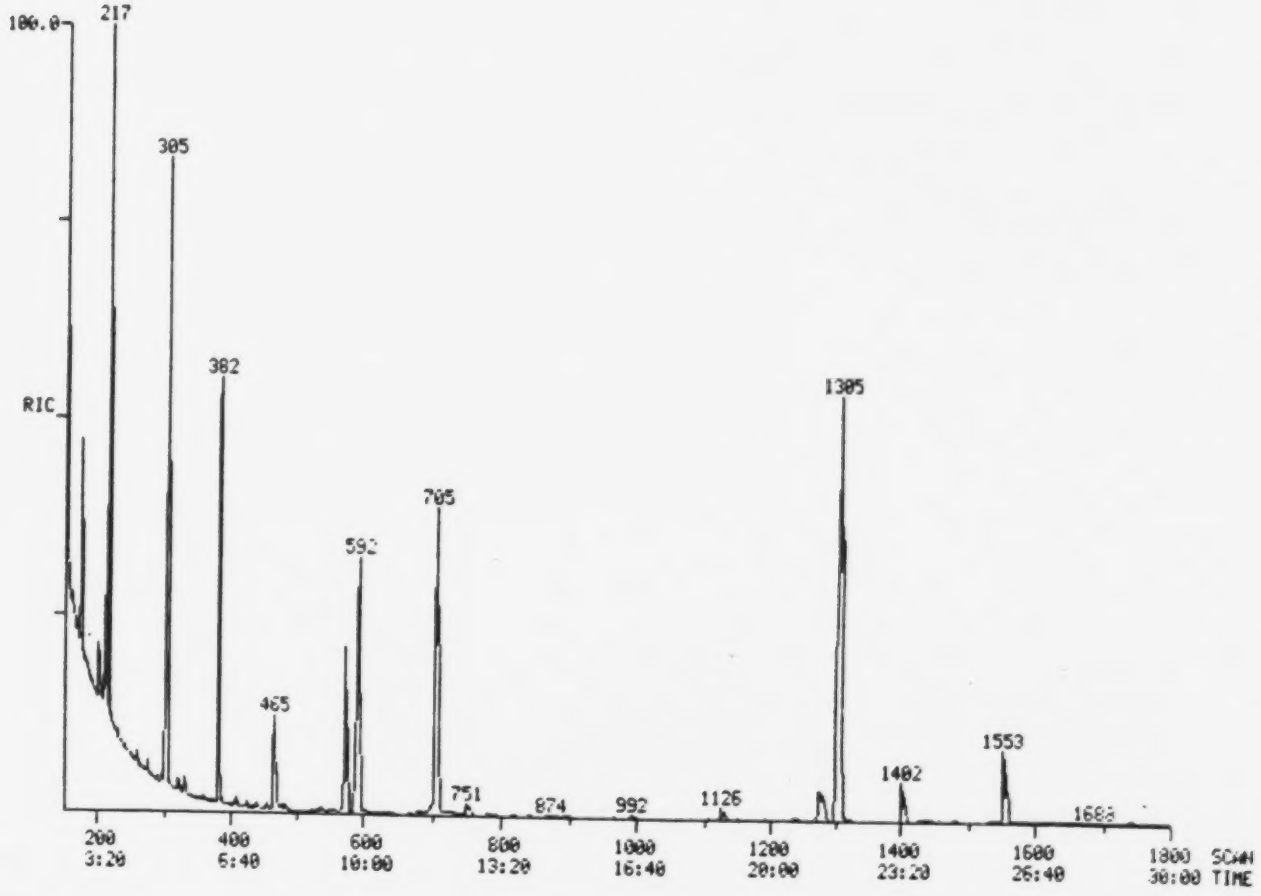


Figure C-2. Reconstructed gas chromatogram of a representative XAD-2® extract (normalized beyond the elution of the solvent peak). Peaks are identified in Table C-1. Very few extraneous peaks are observed, and the extraneous peaks which are identified arise more probably from contamination than from artifact formation.

TABLE C-1. COMPOUNDS IDENTIFIED IN ANALYSES OF XAD-2® EXTRACTS

cd-b XAD compound (scan)	abcd-b XAD compound (scan)	acde-b XAD compound (scan)
Chloroform (126)	Chloroform (140)	Cyclohexane (138)
1-Hexanol (138)	Hexanol (154)	1,4-Dioxane (155)*
2-Hexanol (180)	1,4-Dioxane (175)*	Hexanol (182)
d_8-Toluene (184)†	d_8-Toluene (213)†	Toluene (189)*
Toluene (187)*	Toluene (217)*	Chlorobenzene (262)*
Chlorobenzene (259)*	Chlorobenzene (305)*	Tetrachloroethane (223)*
Xylene (287)	Xylene (331)	Xylene (291)
Tetrachloroethane (346)*	Tetrachloroethane (382)*	Tetrachloroethane (350)*
Phenol (439)*	Phenol (465)*	Phenol*, d_5-Phenol† (444)
Hexachloroethane (556)*	Unknown (408)	Siloxane, column artifact (463)
Nitrobenzene (577)*	Hexachloroethane (571)*	Hexachloroethane (559)*
Naphthalene (695)*	Nitrobenzene (592)*	Nitrobenzene (580)*
Dimethyl phthalate (990)	Naphthalene (705)*	Naphthalene (699)*
Diethyl phthalate (1125)	Benzothiazole (751)	Benzothiazole (748)
Pentachlorophenol (1276)*	Diethyl phthalate (1126)	Dimethyl phthalate (993)
Methyl pentadecanoic acid, methyl ester (1401)	Pentachlorophenol (1276)*	Diethyl phthalate (1128)
Heneicosanoic acid, methyl ester (1552)	Methylpentadecanoic acid, methyl ester (1402)	Pentachlorophenol (1281)*
Unknown (1738)	Methylheptadecanoic acid, methyl ester (1553)	d_{10}-Anthracene (1307)§
d_{10}-Anthracene (1304)§	3-Methyl-2,6-dioxo-4 hexenoic acid (1740)	Methylpentadecanoic acid, methyl ester (1404)
	d_{10}-Anthracene (1305)§	Methylheptadecanoic acid, methyl ester (1556)

* Compounds spiked on XAD-2®.

† Deuterated surrogate compounds.

§ Quantitation standard.

other adsorptive media are abundant, but only specific recoveries for compounds of interest are reported in the literature. For most experiments, if recovery from XAD-2® for a compound of interest is not good, another medium which exhibits better recoveries is used instead of XAD-2 and reasons for poor recovery are not explored. However, observation of artifacts from XAD-2 are reported under certain conditions of extraction.

R.L. Hanson et al. (Evaluation of Tenax-GC® and XAD-2® as Polymer Adsorbents for Sampling Fossil Fuel Combustion Products Containing Nitrogen Oxides. R.L. Hanson, C.R. Clark, R.L. Carpenter, and C.H. Hobbs. Environ. Sci. Technol., 15, 701-705 (1981)) observe that both of the polymers examined decompose in the presence of oxides of nitrogen which are present in combustion effluent streams. Compounds reported from NO exposure include benzoic acid, ethylbenzaldehyde, dimethylbenzaldehyde, ethylphenylethanone or C_5-alkylbenzene, dimethylbenzoic acid, C_3-alkylbenzoic acid, hydroxnitrobenzoic acid, diethyl phthalate, diphenoxybenzene, and dibutyl phthalate. Compounds reported for NO_2 exposure included benzoic acid, ethylbenzaldehyde, C_4-alkybenzene, nitrophenol, ethylbenzoic acid, ethyl benzoate or ethoxyethylbenzene, and dinitrotoluene. None of these compounds were observed in the data from the Radian generator study, but most of the oxygen-containing compounds were observed in the qualitative analysis of the mass spectral data obtained from the Sauget field study (See Appendix F). None of the nitrated compounds, however, were observed in the field study, and no exhaustive examination of the Sauget data has been performed to determine if the oxygenated compounds are restricted to XAD-2® extracts.

R. Care et al. (On the Limits of Detection of Traces of Volatile Organics in Water, Using Amberlite XAD-2® Resin. R. Care, J.D. Morrison, and J.F. Smith. Water Res., 16, 663-665 (1982)) find that cleaned XAD-2® resin continues to release a large number of volatile organic compounds, mainly aromatic hydrocarbons, at low concentrations when extracted with ether after water is passed through the resin. The water appears to release these compounds. Although water was not used directly in the XAD-2® preparation or extraction process in either the generator study or the Sauget field study, relatively large amounts of water were

trapped by the XAD-2® resin. Again, no significant amounts of aromatic hydrocarbons were observed in the data obtained in the generator study, but the qualitative analysis of the Sauget field data shows extensive numbers of alkylated aromatic hydrocarbons which could be released from the XAD-2®, present in the combustion products from the stack, or both.

H.A. James et al. (Impurities Arising from the Use of XAD-2® resin for the Extraction of Organic Pollutants in Drinking Water, H.A. James, C.P. Steel, and I. Wilson. J. Chromatogr., 208, 89-95 (1981)) observe a series of n-alkanes (C_{10} - C_{24}) as a series of impurities. When no water was used in the overall procedure, these compounds could be eliminated. The authors conclude that the impurities come from the resin but are released from the resin only when the resin is in contact with water. Again, no significant amounts of n-alkanes are observed in the examination of the generator data, but these compounds are observed in the qualitative analysis of the Sauget field data, possibly due to the amounts of water entrapped in the XAD-2® resin or possibly as combustion products.

In one report (Collection and Recovery of Organics from Water Using XAD-2® and XE-347 Resins. EPA-600/9-81-018) a small systematic study of recovery of a few types of organic compounds by solvent extraction from XAD-2® resin was reported, and the general trends are consistent with our observations from the generator study. The summary is shown below.

Compound	Recovery by extraction from XAD-2® resin (percent)
1,2,3-Trichloropropane	73
Naphthalene	75
Diethyl phthalate	78
Acridine	91
Phenol	38
Dodecane	15
Pyrrole	1

These results are consistent with our observations that the more polar, water-soluble compounds recover more poorly than non-polar compounds which are not water-soluble. For example, pyridine and pyrrole, chemically similar compounds, both exhibit very poor recoveries for reasons as yet unknown.

Formation of NO_x Artifacts in Aqueous Sample Fractions

An analysis of variance for the laboratory flue gas generator data set indicated that increases in flue gas NO_x levels were associated with decreases in the recoveries of 1,4-dioxane, urethane, and phenol in the aqueous compound fractions of the Semi-VOST train.

If nitration is a route of loss of spiked compounds, nitrophenols would be the products of the reaction for phenol and these compounds should be found in the back components of the sampling train. Accordingly, several extracts of back train components from the generator study were examined for the presence of nitrophenols. No traces of mono- and dinitrated phenols were found. However, the chromatographic elution of nitrophenols are poor. Further analyses of the generator data sets are warranted to evaluate NO_x-compound interactions with urethane and 1,4-dioxane.

CONCLUSIONS

On the basis of the data from the Radian generator study, the conclusion can be drawn that artifact formation is not a significant process. Analysis of XAD-2® extracts shows no significant peaks which can be interpreted as arising from the formation of artifacts. None of the compounds reported as possible XAD-2® artifacts in the literature were observed in the data from the generator study. However, most of the XAD-2® artifacts reported in the literature were formed because of significant amounts of water in the preparation/extraction process, and no water was used in the extraction of the XAD-2® for the generator study.

APPENDIX D
ANALYTICAL PRECISION AND BIAS

INTRODUCTION

In determining the overall precision of the Semi-VOST procedure, it is instructive to examine the precision of each step which may significantly affect the overall precision. The Semi-VOST procedure may be generalized as shown in Figure D-1 consisting of a sampling step, generally done at a site in the field; a sample preparation step; and an analysis step. The latter two steps are done in the laboratory.

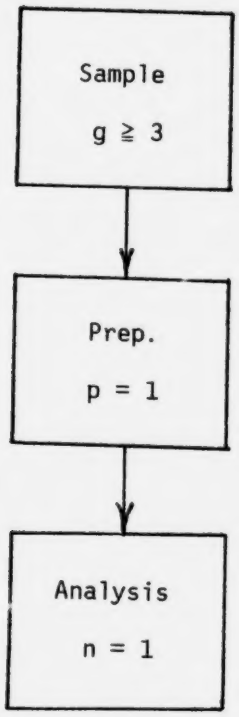
In Figure D-1, g is the number of samples taken and is usually three or greater. The samples may be taken simultaneously or consecutively. Each method introduces a different and characteristic set of variabilities. The number of sample preparations per sample, p, is usually 1, and in the case of the Semi-VOST procedure involves extraction of the XAD-2® resin and Kuderna-Danish (K-D) concentration. The number of analyses per sample preparation for the Semi-VOST process is n. The Semi-VOST analysis is specified to be done on a gas chromatograph/mass spectrometer (GC/MS). Other symbols in Figure D-1 are defined below:

X_i = an analytical determination, i;

$\bar{X}$ = the mean analytical result = $\sum_{i=1}^{N} X_i/N$;

N = npg, the total number of analytical determinations;

s_x^2 = the estimated variance of the analytical determinations = $\sum_{i=1}^{N} (X_i-\bar{X})^2/(N-1)$;



$$\text{Var. } (\bar{X}) = \frac{s_x^2}{npg} = \frac{s_G^2}{g} + \frac{s_p^2}{pg} + \frac{s_A^2}{npg}$$

$$\text{Var } (X_i) = s_x^2 = nps_G^2 + ns_p^2 + s_A^2$$

$$\bar{X} = \sum_{i=1}^{N} \frac{N_i}{N};\ N = npg;\ s_x^2 = \sum_{i=1}^{N} \frac{(X_i - \bar{X})^2}{N-1}$$

Figure D-1. Generalized Semi-VOST procedure.

$\text{Var}(\bar{X})$ = the variance of the mean value of X_i;

$\text{Var}(X_i)$ = the variance of X_i;

s_p^2 = the estimated variance of the preparation step(s);

s_A^2 = the estimated variance of the analytical determinations; and

s_G^2 = the estimated variance of the sampling step.

Four sets of studies were conducted to determine the components of variance described above. These studies are diagrammed schematically in Figure D-2. The Minimum Detection Limit (MDL) study provided the GC/MS estimates for the analytical variance, s_A^2. These studies were done first and were replicated six to eight times at each of four concentrations. The second set of studies was designed to determine the sample preparation variance, and is shown in Figure D-2 as the "Semi-VOST Analytical Precision Laboratory Evaluation." The third study is labeled the "Generator Study" and was conducted in the laboratory to determine the effects of several variables (moisture, sample volume, organic concentration, NO_x concentration, and sample flow rate). The generator study also provided a sampling variance estimate s_G^2 when combined with the MDL analytical variance and sample preparation variances, as described below.

The final set of measurements was taken in the field study and provided a measure of overall method precision as well as a typical field sampling variance estimate. The results and methods of calculation are described below.

In determining an overall precision for the Semi-VOST procedure, the results for chlorobenzene were examined in detail in all the studies described above because chlorobenzene was detected in all the field study samples taken for determining method precision.

SUMMARY PRECISION RESULTS

Summary precision results are given in Table D-1 for chlorobenzene. The overall variability is separated into three components - sampling, sample preparation, and GC/MS analysis - in terms of percent of total variance and percent CV for each component. For the Analytical Laboratory

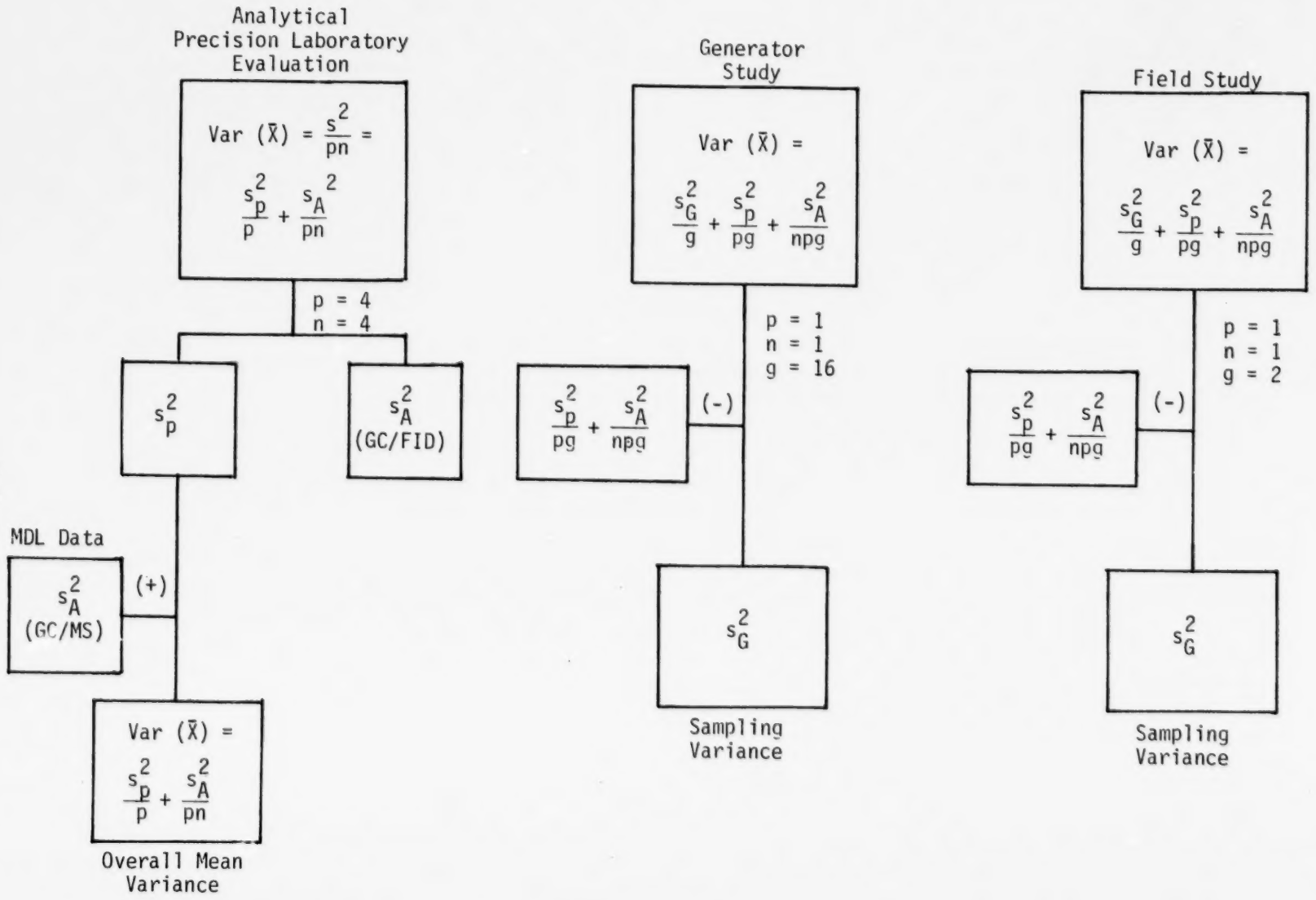


Figure D-2. Separation and combination of components of variance.

TABLE D-1. APPORTIONMENT OF METHOD PRECISION FOR CHLOROBENZENE

	Analytical Laboratory Precision Evaluation with GC/MS			Generator study		Field study	
	% Total variance*	% Total variance†	% CV*,§	% Total variance	% CV	% Total variance	% CV
Sampling	-	-	-	11.4	3.8	78.5	17.1
Sample preparation	6.4	21.6	2.7	5.7	2.7	1.4	2.3
GC/MS analysis	93.6	78.4	10.2	82.9	10.3	20.1	8.6
Overall	100.0	100.0	11.6	100.0	11.3	100.0	19.9

Assumptions:

- GC/MS analytical variance from MDL study applicable in these studies.
- GC/MS instrument response linear function of composition.
- GC/MS sample variance linear function of composition.
- (Sample preparation variance/GC/MS analytical variance) = constant for p = 1, n =1.

* Number of preparations, p = 1; number of analyses per preparation, n = 1.

† Number of preparations = 4; number of analyses per preparation = 4.

§ % CV is percent coefficient of variation = $(s_x/\bar{X}) \times 100$.

Precision Evaluation (four preparations with four analyses per preparation) using the GC/MS analytical variance estimate, the overall precision was 11.6 percent in terms of percent CV. Table D-1 indicates that if the Analytical Laboratory Precision Evaluation was determined with four preparations and with four analyses per preparation, the percentage of the total variance that would be due to the preparation is 21.6 percent, while the GC/MS analytical variance would be 78.4 percent of the total variance. For the preparations and analyses used in the generator study and in the field study, the number of preparations per sample and analyses per preparation are both one. The preparation variance is 6.4 percent of the total variance, while the GC/MS analytical variance would be 93.6 percent of the total variance. The ratio of these two variances (6.4/93.6) was assumed to be constant for chlorobenzene for the generator study and for the field study.

The overall precision estimates for the generator study and the field study were 11.3 and 19.9 (percent CV), respectively. Sampling variance increased from 11.4 to 78.5 percent of the total variance when comparing the generator studies with the field studies. Percent CV is not additive within a particular study, but percent of total variance is additive.

MDL DETERMINATION

The MDL was determined by GC/MS analysis for a mixture of 12 compounds in methanol. The results are given in Table D-2. The method of Glaser, et al. [Glaser, John A., Denis L. Foerst, Gerald D. McKee, Stephen A. Quave, and William L. Budde, "Trace Analysis for Wastewaters," Environmental Science and Technology, 15, (12), 1426 (1981)] was followed in determining MDL. The 12 compounds were mixed in a solution of methanol at an estimated MDL of about 25 ng/μL for each compound. Seven replicate analyses were performed on the GC/MS. Based on the means and standard deviations of the area counts for each compound, a newly estimated MDL was calculated using Glaser's method for each compound and a new solution was mixed at the newly estimated MDL. Four successive iterations were performed, each at a lower concentration for each compound. Glaser's MDL determination is based on the hypothesis that as the concentration decreases,

TABLE D-2. MINIMUM DETECTION LIMIT (MDL) FOR GC/MS ANALYSIS OF TEST COMPOUNDS IN METHANOL

	ng/μL
1,4-Dioxane	7.0
Pyridine	8.5
Toluene	1.9
Urethane	10.0
Chlorobenzene	0.37
1,1,2,2-Tetrachloroethane	0.25
Phenol	5.0
Hexachloroethane	0.90
Nitrobenzene	1.1
Naphthalene	0.32
Resorcinol	7.3
Pentachlorophenol	4.2

the variance of the response variable (i.e., area counts for the GC/MS) increases. For the GC/MS and all the 12 compounds used in this study, the standard deviation (square root of the variance) decreased as the concentration decreased, as can be seen in Table D-3 for chlorobenzene. As a result, Glaser's definition of MDL was modified, and is given in Equation D-5 below.

Part of Glaser's procedure involved injecting solvent blanks between each of the replicate analyses. A maximum blank peak was read in the scan range for each compound in each solvent blank. Thus, a mean, $\bar{X}_B$, and standard deviation, s_B, of seven replicate blank readings were determined for each compound. The maximum blank readings and the sample readings for each compound were assumed to be normally distributed. Figure D-3 shows the distributions of the blanks and samples plotted on a horizontal concentration scale. The variables are defined below Figure D-3 and MDL is defined in Equation D-5.

To calculate X_{CB}:

s_B = standard deviation of peak heights for blank readings,

s_S = standard deviation of peak heights for sample readings,

n_B = number of replicates for blank readings,

n_S = number of replicates for sample readings, and

$t_{(n-1),(1-\alpha)}$ = Student's t statistic with (n-1) degrees of freedom and α level of significance.

$$t_{(n_B-1),\ 0.99} = \frac{X_{CB} - \bar{X}_B}{s_B/\sqrt{n_B}} \qquad \text{(D-1)}$$

$$X_{CB} = \bar{X}_B + t_{(n_B-1),\ 0.99}\ s_B/\sqrt{n_B} \qquad \text{(D-2)}$$

Similarly, to calculate X_{CS}:

$$X_{CS} = \bar{X}_S + t_{(n_S-1),\ 0.99}\ s_S/\sqrt{n_S} \qquad \text{(D-3)}$$

At MDL, $X_{CS} = X_{CB} = X_C$, or $(X_{CS} - X_{CB}) = 0$

$$\bar{X}_B + t_{(n_B-1),\ 0.99}\ s_B/\sqrt{n_B} = \bar{X}_S - t_{(n_S-1),\ 0.99}\ s_S/\sqrt{n_S} \qquad \text{(D-4)}$$

TABLE D-3. GC/MS CHLOROBENZENE RESULTS

Run no.	X ng/μL	$\bar{Y}$ mean area count	Std dev, area count, s	% CV	n	$\hat{Y}$*	$\hat{s}$†	% CV§
1	26.85	19,074.0	2,314.1	12.1	7	19,106.2	1,705.0	8.92
2	8.70	6,148.0	557.5	9.07	8	6,148.3	559.9	9.11
3	1.34	895.9	114.0	12.7	7	893.7	95.58	10.69
4	0.225	95.83	9.24	9.64	6	97.7	25.23	25.82

Using only Runs 2, 3, and 4:

$$\hat{Y} = -62.92930897 + 713.9325793X$$

Correlation coefficient, R = 0.999999809

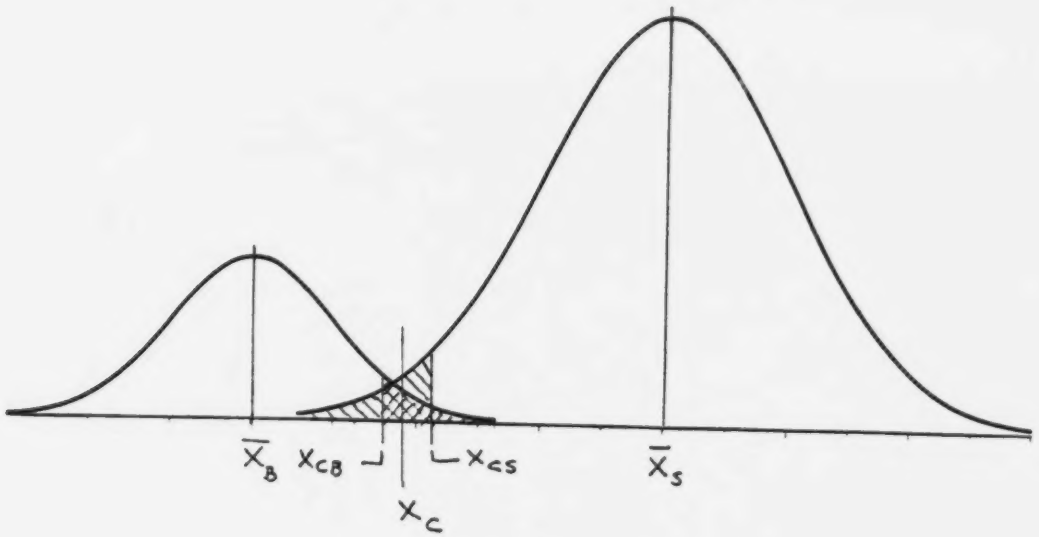
$$\hat{s} = 11.0404616 + 63.08997713X$$

Correlation coefficient,R = 0.998224731

* $\hat{Y}$ denotes value of Y calculated from regression equation given.

† $\hat{s}$ denotes value of s calculated from regression equation given.

§ % CV = $(\hat{s}/\hat{Y}) \cdot 100$.



Given:

$\bar{X}_B$ = mean value of the peak height (or area count) for blank readings,

$\bar{X}_S$ = mean value of the peak height (or area count) for sample readings,

X_{CB} = critical value of the peak height such that P ($X_S \leq X_{CB}$) = 0.99,

X_{CS} = critical value of the peak height such that P ($X_S \geq X_{CS}$) = 0.99,

X_C = critical value of peak heights (at MDL) when $X_C = X_{CS} = X_{CB}$,

Figure D-3. MDL determination.

Define

$$MDL \equiv \bar{X}_S = \bar{X}_B + t_{(n-1),\,0.99}\, s_B/\sqrt{n_B} + t_{(n-1),\,0.99}\, s_S/\sqrt{n_S} \quad \text{(D-5)}$$

B S

The procedure for calculating MDL is outlined below.

1. For each iteration, and for each compound, beginning with the mixture having 25 ng/μL for each component, calculate $\bar{X}_B$, $\bar{X}_s$, s_B, and s_S, the means and standard deviations for the blank readings and sample readings, respectively.

2. Calculate X_{CB} and X_{CS} from Equations D-1 and D-2, respectively. Student's t statistic is tabulated in most statistics texts.

3. For each iteration, calculate $(X_{CB} - X_{CS})$ which can either be positive or negative ($(X_{CB} - X_{CS})$ is shown to be positive in Figure D-3).

4. Plot $(X_{CB} - X_{CS})$ vs. $\bar{X}_S$ and extrapolate (or interpolate) to the $\bar{X}_S$ at which $(X_{CB} - X_{CS}) = 0.0$.

5. MDL is defined as the value of $\bar{X}_S$ when $(X_{CB} - X_{CS}) = 0$.

The variable X_{CS} is calculated by Equation D-2 and is the value of X_S, the peak height (or area count) for a sample reading, such that the probability is $(1-\alpha)$ that all other readings of X_S are greater than X_{CS}. In the definition of MDL in this study, α was chosen to be 0.01. The variable X_{CB} is the value of X_B such that the probability is $(1-\alpha)$ that all other readings of X_B are less than X_{CB}.

For chlorobenzene, more detailed results are given in Table D-3. Columns 2 and 3 of the table are the experimentally determined values of concentration (ng/μL) and mean area counts, respectively. Column 4 gives the standard deviation of the area counts for each run. Column 5 gives the replications per run. Smoothed values of $\hat{Y}$ and $\hat{s}$ were calculated from the regression equations shown. The $\bar{Y}$ and s values for Run 1 were not used in the regression equations for estimation of percent

CV because the results were negative for $\hat{s}$, at $x = 0.225$ ng/μL, which is not realistic. The significant results of this study are that both s_A and percent CV are functions of concentration for chlorobenzene.

LABORATORY ANALYTICAL PRECISION, BIAS, AND SAMPLE PREPARATION EVALUATION

Four test series were performed in this study and are summarized in Table D-4. Standard solutions containing about 260 μg of each of three target compounds (toluene, chlorobenzene, and 1,1,2,2-tetrachloroethane) were spiked into four sets of apparatus as shown in Table D-4. The samples were prepared for analysis either by K-D concentration only for Series 1, or first by extraction followed by K-D concentration for Series 2 and 3. Each apparatus was analyzed by four injections into a GC/FID instrument. Additional details of the tasks are given below.

Series 1 runs involved injecting about 250 μg (260 μg toluene, 266 μg chlorobenzene, and 254 μg 1,1,2,2-tetrachloroethane) of each target compound into about 250 mL of methylene chloride and reducing the volume in a K-D apparatus to less than 5 mL. One hundred microliters of an o-xylene (19.7 μg o-xylene) solution were added as an internal standard to the K-D apparatus concentrate and the solution made up to 5.0 mL with methylene chloride solvent. The solution was then analyzed in quadruplicate using an autosampler to inject the solution into the GC/FID apparatus. Four sets of K-D apparatus were run in Series 1, in parallel.

In Series 2, four sets of XAD-2® resin beds were injected with a nominal 250 μg of each target compound. Each bed was extracted with methylene chloride in a Soxhlet extraction apparatus, and reduced in volume to 5.0 mL using a K-D apparatus. Each K-D concentrate was spiked with 100 μL of the o-xylene internal standard and analyzed in quadruplicate using the autosampler to inject the solution into the GC/FID apparatus.

Series 3 simulated the single set of water impinger extractions in a Semi-VOST apparatus. About 250 μg of each target compound were injected into about 250 mL of water. The water was adjusted to a pH of about 1.0 and extracted with methylene chloride, followed by basic extraction (water pH of 11). The acid and base extracts were combined and reduced

TABLE D-4. LABORATORY PRECISION AND RECOVERY STUDIES

Series	Number of replicates	Standard solution spiked into	Extraction	K-D concentration	GC/FID injection method	Analytical replicates per K-D concentrate
1	4	K-D solution	None	Yes	Autosampler	4
2	4	XAD-2®	Soxhlet	Yes	Autosampler	4
3	4	Water	Separatory funnel	Yes	Autosampler	4
1	4	K-D solution	None	Yes	Manual	4

to 5.0 mL in a K-D apparatus. One hundred µL of o-xylene internal standard were added to each concentrated extract and each was analyzed in quadruplicate, using the autosampler to inject the solution into the GC/FID apparatus.

Series 1 described above was repeated using manual injections into the GC-FID rather than using the autosampler.

Precision and Recovery Results, Laboratory Precision Determination

The precision and recovery results are summarized in Table D-5 for the four sets of procedures described above. The means given in Columns 2 and 3 record the averages of 16 determinations of each compound's recovery for each task (four repeated analyses from each of four sets of apparatus). Column 2 gives the area counts and Column 3 reports the concentrations in µg/mL. Column 4 gives percentage recovery. The amount of each target compound contained in each apparatus in each task is given in the footnote "*" of Table D-1. The percent recovery is calculated by dividing the µg/mL recovered (the mean value in Column 3) by the amount injected (spiked) into each apparatus and multiplying the quotient by 100. This is the only measure of accuracy that was possible in this set of experiments.

Series 1 and 2 all report percent recoveries near 100 percent for all three target compounds. Series 3 involving water extractions, however, shows percent recoveries ranging from 56 to 84 percent.

The analytical variance estimate (and its square root, the standard deviation) was separated from the treatment variance by a standard one-way analysis of variance. The "Treatment" for Series 1 was simply the variance of the K-D concentration step. For Series 2, the "Treatment" standard deviation included the XAD-2® extraction and subsequent K-D concentration to 5 mL. For Series 3, the treatment standard deviation included the separatory funnel extractions, followed by the K-D concentration steps.

Columns 5 and 6 give results of the standard deviation determinations for the GC/FID analyses. Column 5 gives the standard deviations in area counts for the four repeated analyses and the four apparatuses used in each task. Column 6 shows µg/mL determined from the area counts.

TABLE D-5. LABORATORY ANALYTICAL PRECISION AND SAMPLE PREPARATION AND RECOVERY RESULTS

	Mean			GC/FID analysis Std. deviation			Sample preparation Std. deviation		
	Area counts	µg/mL	Percent recovery*	Area counts	µg/mL	Percent CV	Area counts	µg/mL	Percent CV
Series 1, Autosampler Injections (AsI), K-D Concentration + Analysis									
Toluene	42,183	53.2	102.0	307	0.387	0.73	1,717	2.16	4.07
Chlorobenzene	31,134	56.4	106.0	220	0.399	0.71	1,027	1.86	3.30
1,1,2,2-Tetrachloroethane	6,881	55.7	110.0	54	0.437	0.78	245	1.98	3.56
Series 2, AsI, XAD-2® Extraction, K-D Concentration + Analysis									
Toluene	40,114	47.9	92.1	547	0.653	1.36	706	0.84	1.76
Chlorobenzene	31,223	53.6	101.0	244	0.419	0.77	597	1.02	1.88
1,1,2,2-Tetrachloroethane	6,825	53.3	105.0	55	0.429	0.80	141	1.10	2.06
Series 3, AsI, Separatory Funnel Extraction, K-D Concentration + Analysis									
Toluene	27,612	29.2	56.1	196	0.207	0.71	2,457	2.60	8.90
Chlorobenzene	22,680	34.2	64.2	206	0.310	0.91	1,954	2.94	8.61
1,1,2,2-Tetrachloroethane	6,521	42.8	84.3	43	0.285	0.66	505	3.31	7.74
Series 1, Manual Injections, K-D Concentration + Analysis									
Toluene	51,609	46.5	89.5	1,085	0.979	2.10	2,082	1.88	4.03
Chlorobenzene	40,084	52.0	97.7	592	0.768	1.48	1,292	1.65	3.22
1,1,2,2-Tetrachloroethane	8,981	52.5	103.0	102	0.597	1.14	242	1.41	2.69

* Standard solution injected (spiked) into each apparatus contains the following:
Toluene - 260 µg in 5 mL; 52.0 µg/mL
Chlorobenzene - 266 µg in 5 mL; 53.2 µg/mL
1,1,2,2-Tetrachloroethane - 254 µg in 5 mL; 50.8 µg/mL

Column 7 shows the percent coefficients of variation obtained by dividing the analytical standard deviation by the mean recovery, e.g., Column 5/Column 2. This percent CV may be viewed as a precision measurement for the analysis step. The analytical percent CV figures for Series 1, 2, and 3 all appear to average around 0.8 with little variability within or between tasks (with the possible exceptions of toluene in Series 2 and chlorobenzene in Series 3).

The percent CV figures for the analytical standard deviations given in Table D-5 for Series 1, Manual Injections, indicate the analytical standard deviations to be a least twice the analytical standard deviation for Series 1, Autosampler Injections. The increase in percent CVs reflects the increased imprecision caused by manual injections compared to the autosampler injections. The sample preparation standard deviation percent CVs (the last column) for Series 1, Manual Injections, however, compare favorably with those of Series 1, Autosampler Injection runs.

The sample preparation results are given in three forms. Column 8 lists the sample preparation standard deviation area counts which are converted to µg/mL in Column 9. Percent coefficient of variation for the sample preparations in Column 10 gives the quotient of Column 8, the sample preparation standard deviation, divided by the mean area counts, Column 2. The last column in the table is a measure of the precision or variability of the procedure done in the task for a given compound after the analytical variability has been removed. For example, in Series 1 for toluene, the precision of the K-D concentration step is 4.07. The precisions of the K-D concentration step for chlorobenzene and 1,1,2,2-tetrachloroethane are 3.30 and 3.56 percent CV, respectively. As noted above, the precision in Series 1 for the K-D concentration step using manual injections into the GC/FID apparatus is not significantly different from the K-D concentration step when using the autosampler for injections into the GC/FID apparatus. In both cases, handling of the K-D apparatus is identical and a different precision is not to be expected.

For Series 2, the sample preparation standard deviations characterize the variability of the XAD-2® extraction step and K-D concentration step combined. The standard deviations for the extraction-concentration steps for the target compounds in Task C are less than the corresponding

standard deviations for the concentration step alone in Series 2. Testing the hypothesis that for each compound the treatment variances for Series 1 and 2 are equal results in the conclusion that they are equal at the 5 percent level of significance. From a practical viewpoint, the variance of the K-D concentration step alone is not significantly different from the combined XAD-2® extraction and K-D concentration steps. In the calculations below, the standard deviations for each compound for Series 1 and 2 (both done with the autosampler) were pooled for the sample preparation step component of variance.

Sample preparation standard deviations for Series 3 give variabilities and precision measurements for the separatory funnel-K-D concentration steps, after having had the analytical variability removed from the results. These percent CV numbers range from three to five times larger than the Soxhlet extraction-K-D concentration variabilities. This result is not unexpected for at least two reasons: (1) the transfer of an organic compound from the water phase to an organic phase is slow and highly dependent on solubility, contact time, and degree of mixing of the phases, and (2) manual separation of the phases in a separatory funnel is difficult to achieve reproducibly. Obtaining comparable degrees of mixing of two phases in separatory funnels is also difficult to achieve reproducibly. Future experiments will be conducted to determine if multiple separatory funnel extractions improve sample preparation precision and reduce bias.

Because the mean values of the concentrations of toluene, chlorobenzene, and 1,1,2,2-tetrachloroethane for Series 1 are not significantly different from the means for Series 2, and because the treatment standard deviations for the same task are not significantly different, the means and standard deviations were pooled as shown below for chlorobenzene.

For the chlorobenzene mean,

$$\bar{X} = (31,134.3 + 31,223.4)/2 = 31,178.85 \text{ area counts}$$

For the chlorobenzene treatment (or preparation) standard deviation,

$$s_p = \sqrt{(((1,026.9)^2 + (597.1)^2)/2)} = 840 \text{ area counts}$$

The area counts for the analytical standard deviation for chlorobenzene in Table D-3 were not pooled because the analytical standard deviation in the table is for the GC/FID.

In order to determine the percent of the total variability due to sample preparation, a ratio of the sample preparation variance to the total method variance would be required. It was desirable also to determine the percent of the variability due to sampling, sample preparation, and analysis in the generator and field studies for chlorobenzene. Since the latter two studies used GC/MS for analysis, it would be necessary to estimate the GC/MS analytical variance that would have occurred in the laboratory analytical and sample preparation study so that all three studies would be comparable. Figure D-2 diagrams the steps involved. For the laboratory analytical and sample preparation precision and percent recovery evaluation, the overall variance was split into the sample preparation variance, s_p^2, and the GC/FID analytical variance. The GC/MS analytical variance from the MDL studies was then combined with the sample preparation variance to get an overall variance for the study if the GC/MS had been used for the analyses. The calculations involved are given below.

Because the concentration level for chlorobenzene for the laboratory precision and recovery determination runs was outside the range of concentrations in the MDL study, it was necessary to extrapolate the MDL data to determine s_A for chlorobenzene at $\bar{X}$ = 53.2 ng/µL.

The following procedure was used to extrapolate s_A data for GC/MS:

1. calculate $\hat{Y}$ from regression equation, see Table D-3;
2. calculate $\hat{s}_A$ using only the data from Runs 1, 2, and 3;
3. calculate $\hat{s}_A$ using only the data from Runs 2, 3, and 4;
4. correct both values of $\hat{s}_A$ to 31,178.85 area counts for the generator study;
5. pool $\hat{s}_A$ values calculated in Step 4 by taking the geometric mean, round off;
6. calculate percent of total variance attributable to preparation and to analysis for n = 1, p = 1;

7. calculate percent of total variance attributable to preparation and to analysis for n = 4, p = 4; and

8. calculate precision for laboratory precision study for n = 4, p = 4.

The calculations follow and are numbered as indicated in the outline above.

Using Runs 1, 2, 3, and 4, the linear regression equation for chlorobenzene, see Table D-3.

1. @ 53.2 µg/mL, $\hat{Y}$ = 37,855.58388

   actual $\bar{Y}$ = 31,178.85

2. Using only Runs 1, 2, and 3 assuming $s_A = f(x)$

   @ 53.2 µg/mL, $\hat{s}_A$ = 4,554.916811

3. Using only Runs 2, 3, and 4

   @ 53.2 µg/mL, $\hat{s}_A$ = 2,630.185937

4. Correcting both to 31,178.85 area counts gives

   $$\frac{4,554.916811}{37,855.58388} \times 31,178.85 = 3,596.4225$$

   $$\frac{3,367.427245}{37,855.58388} \times 31,178.85 = 2,630.185937$$

5. Pooling estimates (i.e., taking geometric mean) = 3,150.566049

   Round off to $\hat{s}_A$ = 3,200 @ $\bar{X}$ = 31,178.85, % CV = 10.26

   s_p = 840, see above

6. For the case of one preparation and one analysis

   $$\text{Var}(X_i) = s_p^2 + s_A^2$$
   $$= (840)^2 + (3,200)^2$$
   $$= 10,945,600$$

   s_x = 3,308.4 overall variance (one preparation and one analysis)

Calculate proportion of total variance that is preparation for $n = 1$, $p = 1$

$$\frac{(840)^2\ (100)}{10,945,600} = 6.4 \text{ percent due to preparation}$$

Analysis = 93.6 percent due to analysis

7. For the laboratory study $p = 4$, $n = 4$

$$\text{Var } X = s_x^2 = ns_p^2 + s_A^2$$

$$s_x^2 = 4\ (840)^2 + (3,200)^2$$

$$s_x^2 = 13,062,400$$

$$s_x = 3,614.2$$

$$\frac{4\ (840)^2}{(3,614.2)^2} \times 100 = 21.6 \text{ percent preparation}$$

$$\frac{(3,200)^2}{(3,614.2)^2} \times 100 = 78.4 \text{ percent analysis}$$

8. Overall percent $CV = \frac{s_x}{\bar{X}} = \frac{3,614.2}{31,178.85} \times 100 = 11.6$ percent

These results are summarized in Table D-1.

Additional measurements were taken in the laboratory precision and sample preparation studies to determine if a nitrogen blowdown of the SML K-D concentrate from 5 mL to 2.5 mL would adversely change the solute concentrations of toluene, chlorobenzene, and 1,1,2,2-tetrachloroethane. Table D-6 shows the results of the studies. The results in row 1 of the table give the mean GC/FID area counts for the solutes at 5 mL total volume. Dry nitrogen was passed over the solution until the total volume was reduced to 2.5 mL. Eight additional GC/FID analyses were performed and the mean area counts for the solute are given in row 2 of Table D-6. The fact that the ratio of area count (row 2/row 1) was very close to 2.00 (see row 3) confirmed the fact that an insignificant amount of these solutes was lost by the reduction in volume.

TABLE D-6. N_2 VOLUME REDUCTION OF K-D CONCENTRATE

	Toluene	Chlorobenzene	1,1,2,2-Tetrachloroethane
5 mL $\bar{X}$*	30,657	21,431	4,637
2.5 mL $\bar{X}$	60,608	43,127	9,415
Ratio	1.98	2.01	2.03

* $\bar{X}$ = average of eight determinations, area counts.

GENERATOR STUDY PRECISION RESULTS

The generator study precision results are given in Table D-7. For chlorobenzene, the percent CV is 11.30. In the generator study, there were 16 samples, one preparation per sample, and one GC/MS analysis per preparation. For this procedure,

$$\text{Var}\ (\bar{X}) = \frac{s_x^2}{gpn} = \frac{s_G^2}{g} + \frac{s_p^2}{pg} + \frac{s_A^2}{npg} \qquad \text{(D-3)}$$

or

$$\text{Var}\ (X) = s_x = np\ s_G^2 + n\ s_p^2 + s_A^2 \qquad \text{(D-4)}$$

For $n = p = 1$

$$s_x = s_G^2 + s_p^2 + s_A^2 \qquad \text{(D-5)}$$

For the generator study, the mean concentration was

$$X = (1.11 + 3.70)/2 = 2.41\ \text{ng}/\mu\text{L}$$

Using the regression equation in Table D-3,

$$@\ X = 2.41\ \text{ng}/\mu\text{L} \qquad \hat{Y} = 1{,}658.15\ \text{area counts}$$

For generator study precision of 11.30 percent CV, overall

$$s_x = 0.1130\ (1{,}658.15) = 187.37\ \text{area counts}$$

@ X = 2.41 ng/μL, analytical percent CV = 10.29 (see Table D-3)

$$s_A = 0.1029\ (1{,}658.15) = 170.62\ \text{area counts.}$$

Assuming preparation variance/analytical variance = (6.4/93.6)

$$\frac{s_A^2}{s_p^2} = \frac{93.6}{6.4}$$

$$s_p = \sqrt{\frac{(170.62)^2\ 6.4}{93.6}} = 44.65$$

From equation D-5

$$(187.37)^2 = s_G^2 + s_p^2 + s_A^2 = s_G^2 + (44.65)^2 + (170.62)^2$$

$$s_G = 63.27, \text{ the sampling standard deviation}$$

TABLE D-7. GENERATOR STUDY PRECISION*

Compound	Mean recovery, %	Std. dev., %	Precision, % CV
1,4-Dioxane	101	16.6	16.3
Pyridine	62	40.3	65.2
Toluene	94	26.9	29.7
Urethane	49	24.5	49.9
Chlorobenzene	99	11.2	11.3
1,1,2,2-Tetrachloroethane	105	13.3	12.6
Phenol	86	16.7	19.2
Nitrobenzene	111	9.0	8.1
Hexachloroethane	104	7.4	7.1
Naphthalene	107	11.4	10.7
Resorcinol	-	-	-
Pentachlorophenol	-	-	-

* Based on 16 preparations and one analysis for each preparation.

Calculate percent of total variance for each step of the procedure

1. sampling: $\frac{(63.27)^2}{(187.37)^2} \times 100 = 11.4$ percent

2. preparation: $\frac{(44.65)^2}{(187.37)^2} \times 100 = 5.7$ percent

3. GC/MS analysis: $\frac{(170.62)^2}{(187.37)^2} \times 100 = 82.9$ percent

Overall precision 11.30 percent, see Tables D-7 and D-1.

FIELD STUDY PRECISION RESULTS

Table D-8 summarizes the chlorobenzene precision results for the field study. Columns 2, 3, and 4 present the standard deviation, the mean, and the percent coefficient of variation (% CV) for the concentrations, corrected for blanks, of samples for the duplicated run pairs shown in Column 1. The final three columns in the table show the results, corrected for a deuterated spike that was put in the sample train after the completion of the sample and before the sample preparation step or analysis.

Below the chlorobenzene concentration values for runs 5B-5D are pooled values of the standard deviation, the mean, and the resulting percent CV. Pooled values in the row labeled (a) include all runs with the exception of the run pair 4B-4D. Pooled values in row (b) exclude run pairs 4B-4D, 1A-1B, and 2A-2B. The latter two pairs (runs 1A-1B and 2A-2B) were test runs in which a dynamic spike of toluene, chlorobenzene, and 1,1,2,2-tetrachloroethane was introduced into the Semi-VOST sample train by the Radian field crew. The purpose of the dynamic spike was to enable the calculation of a percent recovery of the spike as an accuracy measure.

Because the dynamic spike added to the overall variability of the chlorobenzene measurement, runs 1A-1B and 2A-2B were not included in the overall precision determination. Further, because neither the Generator Study nor the Laboratory Analytical Precision Determination used a deuterated spike, the data in the last three columns of Table D-7 were not used in characterizing the overall field study precision.

TABLE D-8. CHLOROBENZENE PRECISION RESULTS, FIELD STUDY

Run pair	Concentration, µg/m³			Concentration, µg/m³, corrected for deuterated spike recovery		
	Mean	Std. dev.	% CV	Mean	Std. dev.	% CV
1A-1B	69.9	5.41	7.7	69.2	17.2	24.9
1C-1D	65.8	1.57	2.4	71.2	2.12	3.0
2A-2B	88.8	8.00	9.0	152.2	45.7	30.0
2C-2D	61.2	9.59	15.7	72.0	26.4	36.7
3A-3C	80.8	1.86	2.3	92.6	1.85	2.0
3B-3D	93.7	1.76	1.9	100.2	0.40	0.4
4A-4C	102.6	2.86	2.8	102.2	3.60	3.5
4B-4D*	-	-	-	-	-	-
5A-5C	114.0	44.8	39.3	127.6	1.30	1.0
5B-5D	94.7	2.25	2.4	107.7	4.28	4.0
Pooled						
(a)†	85.7	15.7	18.3	99.4	18.6	18.7
(b)§	87.5	17.4	19.9	96.2	10.3	10.7

* Deleted because of sampling problems.

† Pooled (a) values include all run pairs except 4B-4D.

§ Pooled (b) values do not include 1A-1B, 2A-2B, or 4B-4D.

The standard deviations in Column 2 were tested for homogeneity of variance by the Bartlett test and were found not to be homogeneous. Specifically the standard deviation of run pair 5A-5C equal to 44.8 might not be considered as part of a uniform population of standard deviations. This value might be declared to be an outlier and discarded from the data set, except for the fact that when corrected for the deuterated spike, it appears to fall into line with the standard deviations in Column 5 of the table. It is, therefore, not recommended that the value be deleted from the data set as an outlier.

The standard deviations of Column 2 were pooled by the following formula:

$$s_{pooled} = (s^2_{1C-1D} + s^2_{2C-2D} + s^2_{3A-3C} + s^2_{3B-3D} + s^2_{4A-4C} + s^2_{5A-5C} + s^2_{5B-5D})/7)^{\frac{1}{2}}$$

The pooled means were calculated as the arithmetic mean of the mean values. The overall precision in terms of percent coefficient of variation is calculated by:

$$\% \text{ CV} = (s_{pooled}/\bar{X}) \times 100$$

$$= (17.4/87.5) \times 100$$

$$\% \text{ CV} = 19.9 \text{ percent precision}$$

The overall variance for the field study includes the sampling variance, the sample preparation variance, and the analytical variance as follows:

$$\text{Overall } s^2 = s^2_G + s^2_p + s^2_A$$

For the field tests: $\bar{X} = 26.85$ ng/µL

Using the MDL calibration

$$@ \bar{X} = 26.85 \text{ ng/µL}, \quad \hat{Y} = 19{,}704$$

$$s = 0.199 \times 19{,}704 = 3{,}795.7$$

@ X = 26.85, % CV for GC/MS = 8.924 (see Table D-3)

$s_A = 0.08924 \times 19{,}704 = 1{,}702.2$

$s_p = \sqrt{\frac{(1702.2)^2\ (6.41)}{93.59}} = 445.5$

$s_G^2 = 11{,}318{,}357$

$s_G = 3{,}364.3$

Calculate percent of total variance for sampling, preparation, and analytical steps.

Sampling: $\%\ CV = \frac{3{,}364.3}{19{,}704} \times 100 = 17.1$ percent

Preparation: $\%\ CV = \frac{445.5}{19{,}704} = 2.3$ percent

Analysis: $\%\ CV = \frac{1{,}702.2}{19{,}204} = 8.6$ percent

These % CV values characterize to some extent the precision of each step in the procedure.

APPENDIX E
FIELD TEST PROGRAM

Appendix E presents a description of the field testing portion of this program to evaluate the bias and precision of the Semi-VOST method. Included in this appendix are descriptions of the test site, the sampling equipment and sample plan, and a listing of the raw data collected in the field. Sample collection procedures and protocols were presented in Appendix A. An analysis of the field test results is presented in Appendix F and summarized in Chapter 6 of the final report.

TEST SITE DESCRIPTION

Trade Waste Incineration, a division of Chemical Waste Management Inc., operates a hazardous waste incinerator at Sauget, Illinois. The purpose of this incinerator is to destroy hazardous industrial waste other than PCBs and dioxins by combustion at elevated temperatures. The waste streams incinerated are:

1. liquid high Btu - containing mostly waste organic solvents,
2. liquid low Btu - containing water-soluble organic solvents (40 percent organics),
3. slurries and sludges - containing primarily organic sludges and slurries, and
4. solids - containing almost any hazardous material in solid form.

These wastes are injected into the incinerator at varying times to be combusted. The temperature of the incinerator is maintained in the 982-1093°C range. If the feed of one source has insufficient Btu content to maintain this temperature or if a waste stream with too high a Btu content is fed, the operator can switch feed or discontinue feed to allow for a smooth operation.

The process is required to maintain combustion conditions such that the CO emissions are kept below the 50 ppmv threshold level. Both temperature and CO monitors allow the operator to change feeds accordingly.

Figure E-1 is a block diagram of the incinerator process and the control devices. The waste is fed into the primary combustion chamber where it is volatilized and partially combusted at ~982°C. From there, the gaseous stream enters the secondary chamber where the temperature is maintained at ~1093°C with auxiliary fuel. The overall retention time for both chambers is ~5 seconds. The gaseous combustion products exit the combustion chamber and pass through a venturi scrubber, a packed scrubber where ammonia is added to neutralize the hydrochloric acid, a large liquid demister containing coalescing filter pads, and finally exhaust through the stack.

When the incinerator is operated at optimal conditions, the high Btu stream is fed at 5.4 kg per minute and the low Btu stream at 6.8 kg per minute. The slurry stream feed rate is consistent at approximately 4.5 kg per minute. During the field sampling, when solids were fed to the incinerator, the operator stopped the flow of the high Btu and low Btu feeds for approximately 1 minute. After that period, the flow of the low and high Btu streams was reinstated. During this Semi-VOST evaluation study, a normal load was approximately 18 kg of solids every 5 minutes. The solid waste feed to the incinerator during this test period was comprised of hospital waste, vermiculite, rags, and solid materials. Occasionally, waste sulfuric acid was fed although only in small amounts so the ammonia scrubber system would not be overloaded. In addition, small amounts of outdated nitroglycerin tablets were added to most of the solids during Runs 4 and 5.

During Runs 4 and 5, hexachlorocyclopentadiene (C-5,6) was spiked into the high Btu waste stream at approximately 1 percent (weight basis) of the total feed. The level of spiking was determined by taking the maximum feed rates for each stream and calculating the pounds per minute required to give a 1 percent feed rate. During Run 3, the high Btu feed was spiked with dibromomethane at the 1 percent level. During Runs 1 and 2, there was no low Btu stream being fed. The low Btu waste became

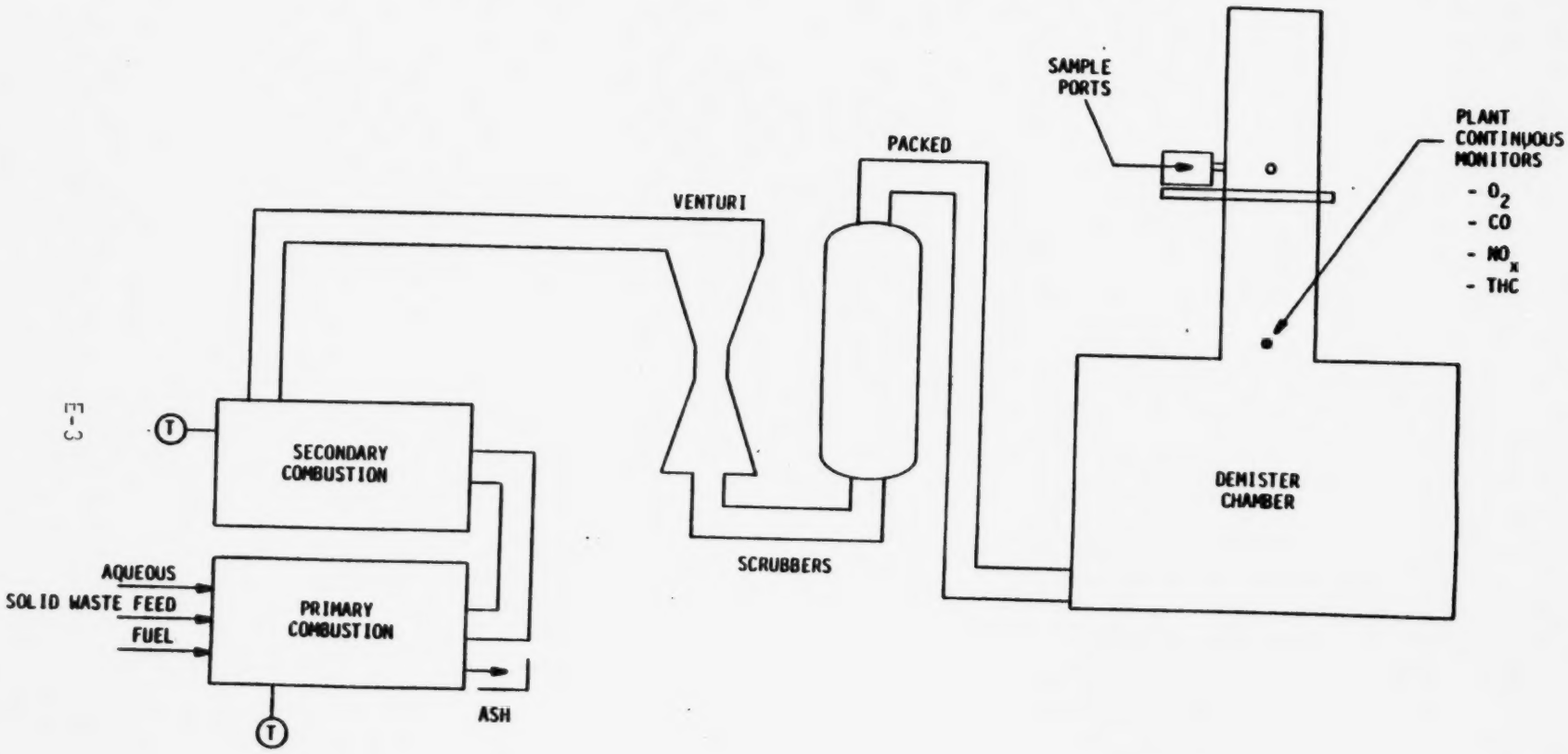


Figure E-1. Trade Waste Incineration incinerator configuration.

available for subsequent runs. The sludge, high Btu waste, and the solids were fed continuously throughout Runs 1 through 5. The feed composition of the waste as supplied by Trade Waste Incineration is given in Table E-1.

Environmental and Plant Conditions During the Test

The tests were conducted during the weeks of February 3 and February 10, 1985. The weather conditions at the plant were extremely adverse. At no time during the testing period did the ambient temperature exceed freezing (0°C). Quite often the wind chill index was below -18°C and went down to -30°C at one point. These conditions provided the worst possible case both for the process and for the sampling. The extreme cold could have been responsible for the partial plugging of the primary chamber exhaust during the first and second runs. The plug was removed the following day along with the clinkers in the primary chamber.

The only other process condition of note was that the sampling stream was supersaturated with water. Water droplets were noticed in the stack during each of the runs, possibly due to the extremely cold temperatures.

SAMPLING EQUIPMENT DESCRIPTION

Each test run was performed with four separate Semi-VOST trains as shown in Figure E-2. Each separate train contained every train component element shown with the exception of the pitot tube and the thermocouple. In order to obtain identical samples of the exhaust stream for each of the trains, a common probe system was used to accommodate all four train systems (quad probe). The quad probe contained four separate probes and nozzles but only two pitot tubes for flow measurements and two thermocouples for temperature measurements. Figure E-3 is a diagram of this quad probe.

Each test series was performed with four trains operating at a single point in the stack. The sampling point chosen was a point of average velocity which was approximately 10.2 cm into the stack. Each train was run isokinetically using the pitot measurements of the pitot closest to the two probes in the stack. For example, the left side of

TABLE E-1. WASTE FEED COMPOSITION

High Btu feed*	Low Btu feed*	Sludge	Solids
Feed rate = 5.4 kg/min	6.8 kg/min	4.5 kg/min	4.5 kg/min
Composition			
Toluene - 4.88 percent 1,1,1-trichloroethane - 10 percent Xylene - 10 percent Isopropyl chloride Glycols Pesticide wastes Cement wastes Paint/ink wastes Various solvents Various chlorinated organics Various organic mixtures	Pesticide manufacturing wastes - 1 percent pesticides in aqueous solution	NA†	NA

* These mixtures were fed from a single tank.

† NA = not available.

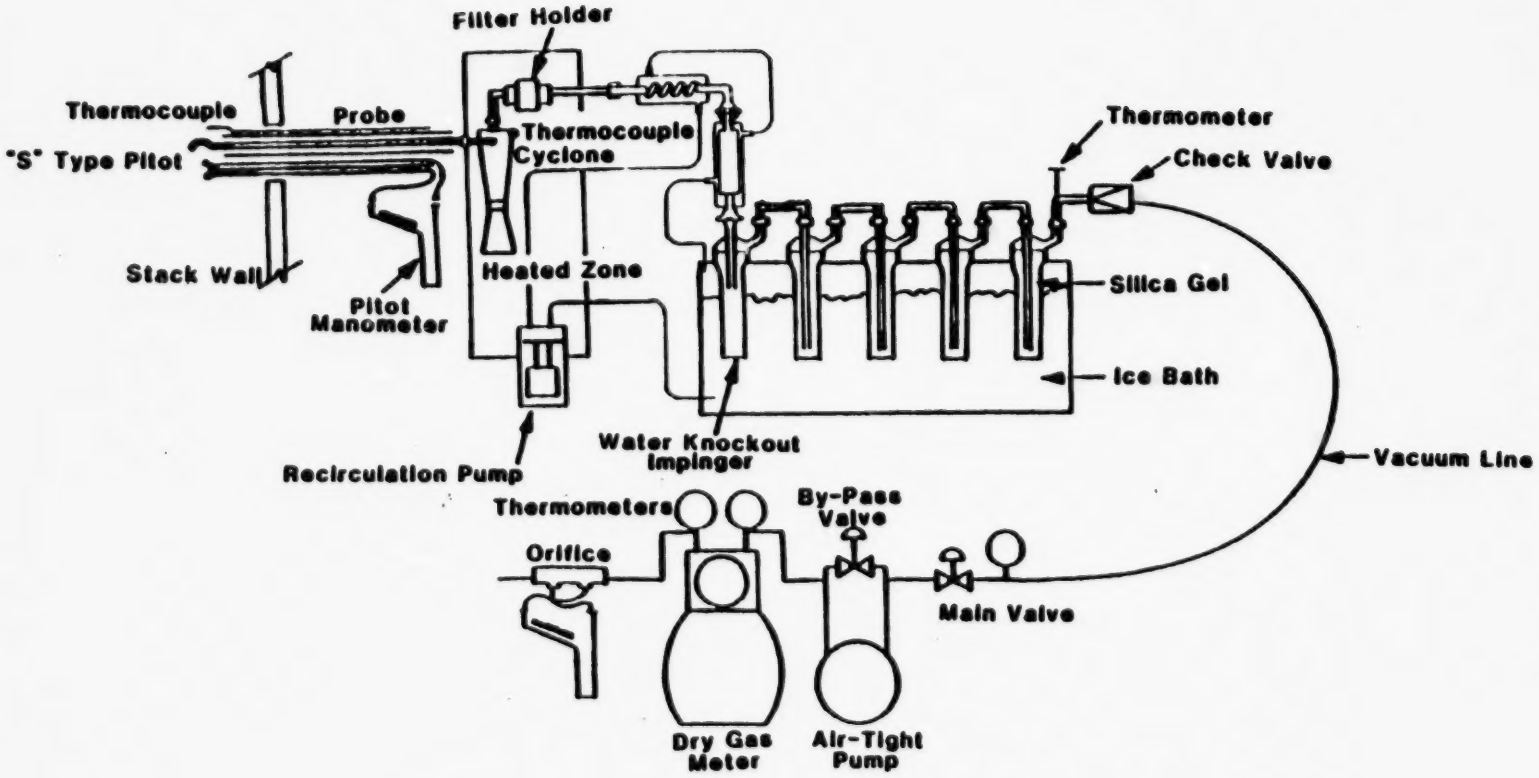


Figure E-2. Semi-VOST train.

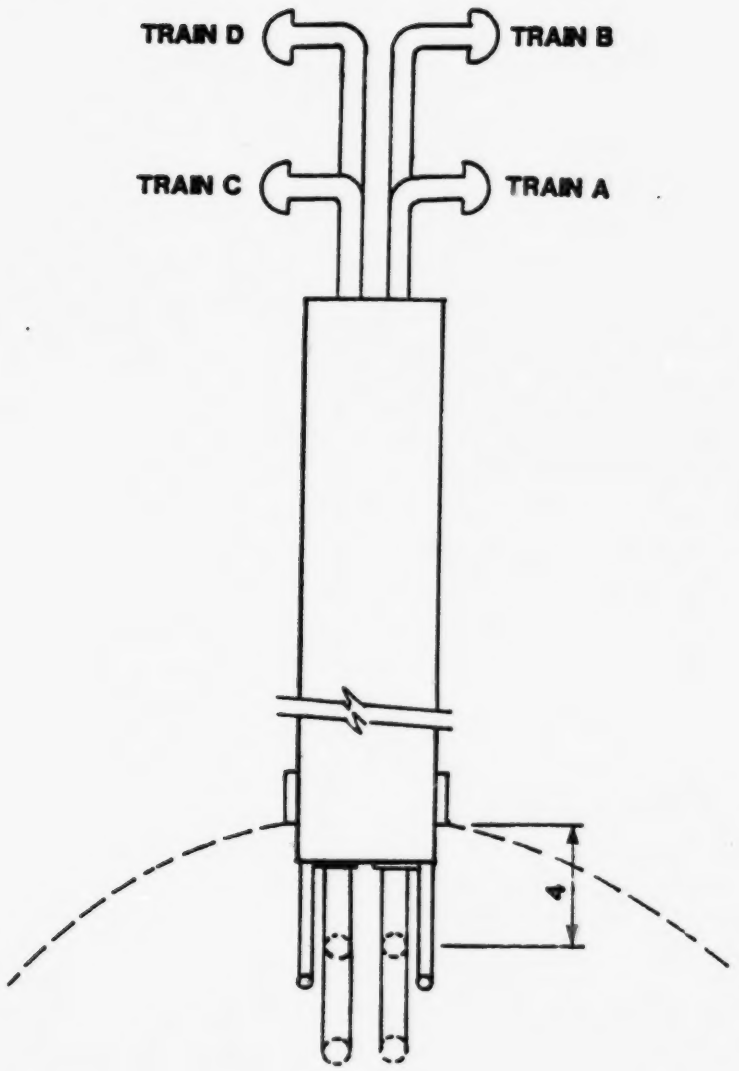


Figure E-3. Quad probe.

the quad probe utilized temperature and flow measurements from the left pitot and thermocouple while the right side utilized the right pitot and thermocouple.

A dynamic spiking system was located on the sampling platform. This system consisted of compressed gas cylinders, regulators, heated lines, mass flow controllers, and glass injection "T's." Figure E-4 shows the spiking apparatus that was used. Both the sampling trains and the spiking equipment were located on a common sampling platform. The entire platform was covered and heated to provide an ambient temperature of approximately 7.2°C.

Semi-VOST Trains

There was no deviation from the method or test plan relative to the train set-up. The probe and filter temperatures were maintained at 121°C as specified in the test plan. With the exception of the specially designed quad probe, the trains were the standard EPA Method 5 trains with a condenser and XAD-2® resin trap added to meet the specifications of Semi-VOST. The probe liners were modified with right angle bends at the ball joint end to facilitate connection to the filter boxes of each train. Trains A and C had shorter probe lengths than Trains B and D. The sampling nozzles conformed to EPA design. However, the nozzles for Trains A and C were shorter than the nozzles for Trains B and D to ensure that all sampling took place on the same plane with no flow disturbances (see Figure E-5).

Spiking Apparatus

The dynamic spiking of the sampling trains with toluene, chlorobenzene, and 1,1,2,2-tetrachloroethane was accomplished utilizing the apparatus shown in Figure E-4. This system was comprised of five flow controllers, two readout devices, and interconnecting tubing. Flow controllers FC-1, FC-2, and FC-3 were delivering preset flows of 88, 13, and 5 cc/min, respectively, for toluene, chlorobenzene, and 1,1,2,2-tetrachloroethane, from compressed gas cylinders. The three gases were mixed at a common point and the stream was split and then directed to flow controllers FC-4 and FC-5. These two flow controllers were set to

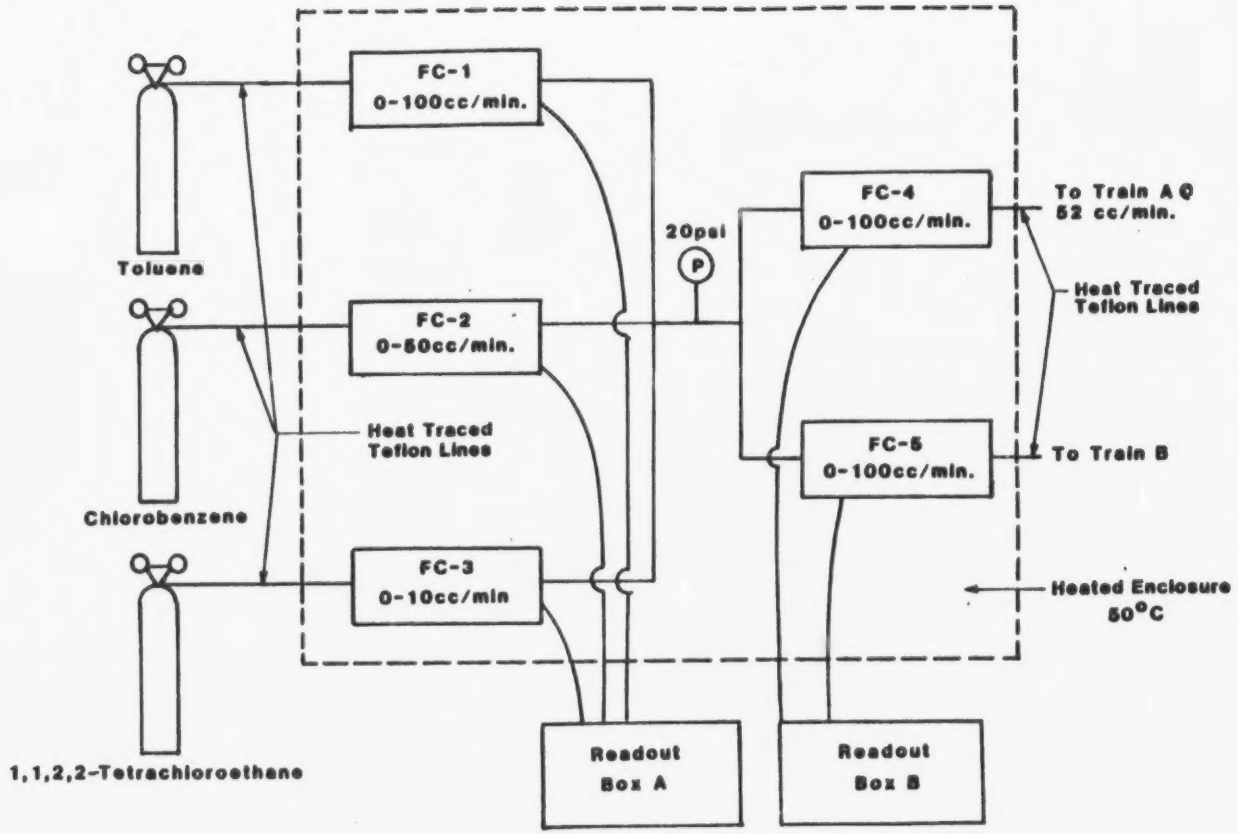


Figure E-4. Dynamic spiking apparatus.

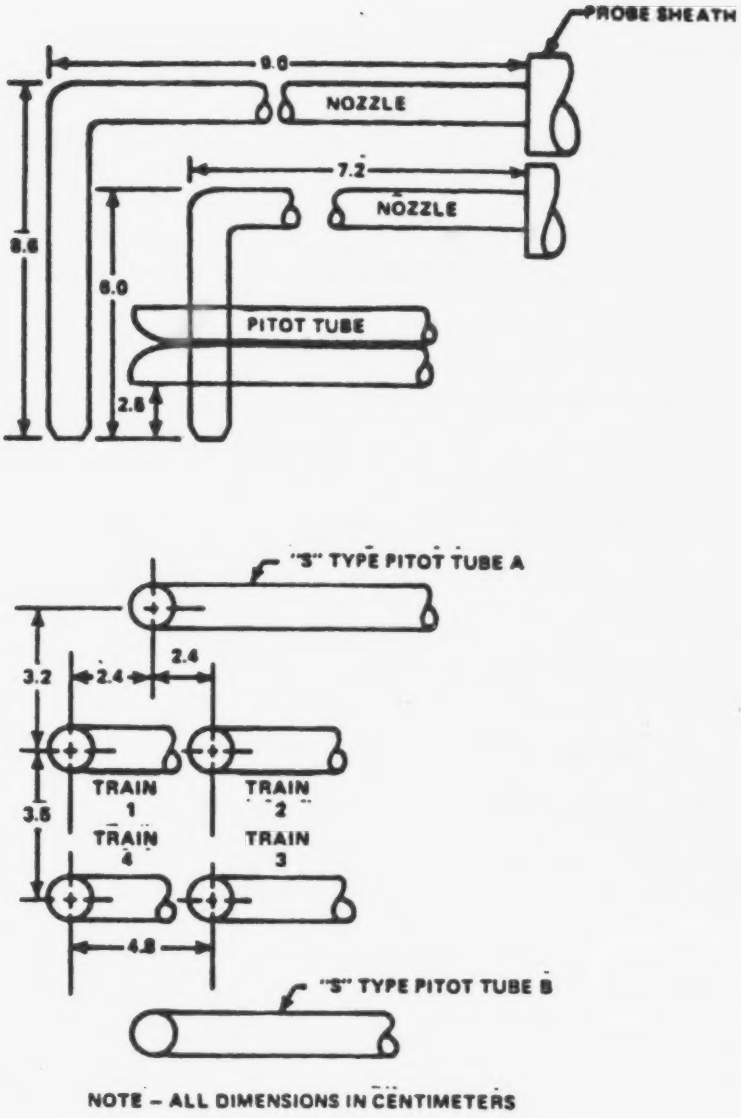


Figure 4-5. Double pitot sampling arrangement: (top) side view; (bottom) upstream view.

deliver 52 cc/min each to Trains A and B during Runs 1 and 2. The gaseous spike entered each train through a glass "T" located after the filter and before the condenser of each train. The Teflon® lines leading from the gas cylinders to the flow controllers and from the controllers to the glass "T" were heat-traced and maintained at approximately 120°C. The flow controller assembly was enclosed and maintained at approximately 50°C. For proper operation, each flow controller required a minimum pressure drop of 1.4 kg/cm^2 (20 psig). The pressure exiting the gas cylinders was maintained at 2.8 kg/cm^2 (40 psig) (above ambient). The pressure prior to FC-4 and FC-5 was 1.4 kg/cm^2 (20 psig), with the exiting gas entering the sampling trains at ambient pressure. Under the preset conditions of pressure and flow, equal volumes of the spiking gas mixture were delivered to the specified sampling trains during the entire sampling period.

The spiking apparatus described above was calibrated and tested in the laboratory prior to this field testing. Flow controllers FC-1, FC-2, and FC-3 were calibrated at 2.8 kg/cm^2 (40 psig) and controllers FC-4 and FC-5 were calibrated at 1.4 kg/cm^2 (20 psig). The results of the preliminary laboratory tests showed that the spiking system required a finite equilibration time before accurate compound delivery could be expected. The optimal time was found to be approximately 2 hours. The minimum equilibration time allowed during these tests was 4 hours.

Field Staging Area

The host plant provided a room for on-site calibration, train preparation, and recovery. One side of the room was used for sample preparation, sample recovery, sample custody, and packaging for shipment to the RTP laboratory. The other side of the room was set up with a GC/FID and a computerized integrating recorder. These instruments were used to calibrate the spiking system prior to and after the spiking tests at the stack. In addition to the GC/FID, a soap film flow meter was set up to check the flows of the mass flow controllers prior to testing.

The staging area was located away from the waste storage area and the analytical laboratory so that possible contamination from external sources in the recovery area was minimized.

"Blank" Trains

A complete train was assembled to serve as a blank for each test. The components of this additional train were chosen at random from the sets of glassware that were shipped to the site. Each piece was assembled in the set-up/recovery area. The complete set of glassware was then transported to the test location with the other glassware and leak-checked at the stack. Following the test, the blank train was leak-checked again and returned to the recovery area where it was disassembled along with the test trains. The series of blanks collected in this manner were called "Train" blanks. Other blanks taken were "Trip" blanks which accompanied the equipment during transportation but were not loaded into a train. These blanks were stored in the staging area.

SAMPLING SCHEDULE

The field test consisted of a series of five runs which were taken on 3 test days. Each test run had four trains (A, B, C, D) connected to the quad probe. The quad probe nozzles sampled from a single point in the stack that was representative of average velocity. During Tests 1 and 2, Trains A and B were spiked with 10 times the minimum detectable level of toluene, chlorobenzene, and 1,1,2,2-tetrachloroethane. The calculations for the amount spiked are the same as for the pretest checkout of the spiking apparatus. Runs 3, 4, and 5 were distributive volume experiments in which Trains A and C were operated for one-half the time of Trains B and D. During Run 3, the time period consisted of 2 hours for Trains A and C and 4 hours for Trains B and D. Runs 4 and 5 were shortened to runs of 1 hour and 2 hours due to plant constraints. Table E-2 presents the testing schedule along with the test parameters for the 5-day test period.

Table E-2. TEST PARAMETERS AND SCHEDULE

TEST PARAMETERS

	Trains A, B	Trains C, D	
Run 1 -	Spiked with 3 organics (toluene, chlorobenzene, 1,1,2,2-tetrachloroethane)	Unspiked	2 h - colocated probes; 0.014 m^3 (0.5 cfm) single point
Run 2 -	Spiked with 3 organics (toluene, chlorobenzene, 1,1,2,2-tetrachloroethane)	Unspiked	2 h - colocated probes; 0.014 m^3 (0.5 cfm) single point
	Trains A, C	**Trains B, D**	
Run 3 -	2 h run	4 h run	0.5 cfm single point colocated probes; 2 filters required for each train
Run 4 -	1 h run	2 h run	0.5 cfm single point colocated probes
Run 5 -	1 h run	2 h run	0.5 cfm single point colocated probes

TEST SCHEDULE

Day 1 - Set up
Day 2 - Runs 1 and 2 (spiking runs)
Day 3 - Recovery (temperature - 22°F, clinkers removed from exhaust)
Day 4 - Run 3, 2 h/4 h distributive volume run
Day 5 - Recovery
Day 6 - Runs 4 and 5 (1 h/2 h distributive volume run)
Day 7 - Recovery/pack
Day 8 - Travel

APPENDIX F
FIELD TEST ANALYTICAL DATA

GC/MS CALIBRATION/INSTRUMENT CONDITIONS

Extracted samples were analyzed on a Finnigan 5100 gas chromatograph/mass spectrometer/data system. Operating conditions are shown in Table F-1. Decafluorotriphenylphosphine (DFTPP) was used to establish tuning criteria according to Table F-2. A Supelco column performance mixture containing octanone, decane, 1-octanol, undecane, 2,6-dimethylphenol, 2,6-dimethylaniline, naphthalene, dodecane, and tridecane was used weekly to monitor acceptability of column performance. Column performance data are reported in Appendix G. A five-point calibration curve was prepared in triplicate.

The concentration levels for surrogate compounds (d_8-1,4-dioxane, d_5-pyridine, d_8-toluene, d_5-chlorobenzene, d_5-phenol, d_5-nitrobenzene, d_8-naphthalene, and $^{13}C_6$-pentachlorophenol) and target compounds (toluene, chlorobenzene, and 1,1,2,2-tetrachloroethane) were 10, 25, 50, 100 and 200 ng/uL. The quantitation standard, d_{10}-phenanthrene, was held constant at 100 ng/uL. For some of the compounds, the entire range of calibration standards did not produce points which could be used to generate a calibration curve because of saturation of the ions of the compounds at the higher concentration levels. A fifteen-point calibration curve requires approximately two days to generate. Data for a five-point calibration curve (a single injection at each concentration level) and the fifteen-point calibration (triplicate injections at each concentration level) are shown in Table F-3. Values obtained for calibration samples analyzed twice daily and control charts are shown in the Quality Control Section (Appendix G). The five-point calibration can be generated in one day of analysis, and the relative percent difference between the five-point and the fifteen-point calibration values exhibits a small change. The additional replicates do often improve the precision of the

Table F-1. OPERATING CONDITIONS GC/MS ANALYSIS OF EXTRACTED SAMPLES

Instrument	Finnigan 5100 Gas Chromatograph/Mass Spectrometer/Data System
Column	30m wide-bore (0.32 mm) thick film (1 u) DB-5 fused silica capillary
Carrier gas	Helium
Split flow	15 mL/min
Septum sweep	3 mL/min
Column head pressure	(0.8 kg/cm^2) 10.8 psi
Injector temperature	300°C
Transfer line oven	270°C
Injection conditions	Splitless 0.6 min, then split
GC temperature program	40°C for 4 min, then 10°C/min to 270°C and hold for 20 min
Electron energy	70eV, nominal
Ionization conditions	Electron ionization
Mass range	35-500 daltons
Scan cycle	1 sec

TABLE F-2. DFTPP KEY MASSES AND ABUNDANCE CRITERIA

Mass	m/z Abundance criteria*
51	30-60 percent of mass 198
68	Less than 2 percent of mass 69
70	Less than 2 percent of mass 69
127	40-60 percent of mass 198
197	Less than 1 percent of mass 198
198	Base peak, 100 percent relative abundance
275	10-30 percent of mass 198
365	Greater than 1 percent of mass 198
441	Present but less than mass 443
442	Greater than 40 percent of mass 198
443	17-23 percent of mass 442

* Federal Register, Vol. 49, No. 209, Friday, October 26, 1984.

TABLE F-3. CALIBRATION CURVES FOR QUANTITATIVE ANALYSIS

Compound	Ion	5 Points			15 Points			Relative percent difference*
		Mean response factor	Standard deviation	Coefficient of variation	Mean response factor	Standard deviation	Coefficient of variation	
d_{10}-phenanthrene	160	1.000	0	0	1.000	0	0	--
	188#	--	--	--	--	--	--	--
d_8-1,4-dioxane	62	0.437	0.027	6.1	0.472	0.029	6.1	7.4
	96	1.268	0.105	8.3	1.359	0.088	6.5	6.7
d_5-pyridine	52	1.339	0.058	4.3	1.426	0.076	5.3	6.1
	84	3.280**	0.136	4.1	--	--	--	--
d_8-toluene	54	0.839	0.056	6.6	0.899	0.052	5.8	6.7
	70	0.949	0.053	5.5	1.025	0.058	5.6	7.4
	98	5.591**	0.188	3.4	--	--	--	--
d_5-chlorobenzene	54	1.701	0.213	12.5	1.851	0.114	6.2	8.1
	117	4.181**	0.179	4.3	4.345**	0.250	5.8	3.8
	119	1.263	0.141	11.2	1.374	0.079	5.7	8.1
d_5-phenol	71	1.675	0.370	22.1	1.819	0.149	8.2	7.9
	99	3.866**	0.509	13.2	3.730**	0.364	9.8	3.6
d_5-nitrobenzene	98	0.388	0.013	3.2	0.409	0.030	7.2	5.1
	128	1.057	0.092	8.7	1.102	0.137	12.4	4.1
d_8-naphthalene	108	1.049	0.170	16.2	1.124	0.071	6.3	6.7
	136	7.97**	1.385	17.4	8.329##	1.374	16.5	4.3
$^{13}C_6$-pentachlorophenol	270	0.306	0.045	14.8	0.311	0.050	16.2	1.6
	272	0.490	0.059	12.0	0.499	0.077	15.4	1.8
toluene	51	0.816	0.075	9.2	0.858	0.058	6.8	4.9
	65	1.193	0.074	6.2	1.279	0.068	5.3	6.7
	91	6.744**	0.271	4.0	7.012**	0.381	5.4	3.8
chlorobenzene	51	1.621	0.215	13.2	1.771	0.112	6.4	8.5
	112	4.094**	0.181	4.4	4.229**	0.220	5.2	3.2
	114	1.217	0.132	10.8	1.329	0.072	5.4	8.4
1,1,2,2-tetrachloroethane	83	4.078**	0.409	10.0	4.274	0.386	9.1	4.6
	131	0.294	0.033	11.3	0.310	0.019	6.0	5.2
	168	0.186	0.023	12.1	0.199	0.012	6.2	6.5

* Calculated as $\frac{RF_5 - RF_{15}}{RF_{15}}$ where RF_5 = mean value for five data points and RF_{15} = mean value for 15 data points.

Molecular ion (m/z 188) of d_{10}-phenanthrene saturated at 100 ng/uL so a fragment ion (m/z 160) was used.

** The ion was saturated at 100 and 200 ng/uL, so the mean represents 10, 25, and 50 ng/uL for this ion only. Other ions for the compound provided usable values through the entire concentration range.

Eight usable data points.

determination, as illustrated by the change in the percent coefficient of variation exhibited by the ions of d_5-phenol (22.1 vs. 8.2 and 13.2 vs. 9.8) but the improvement is not a consistent trend for all ions of all compounds. The mean values from the fifteen-point calibration data base were used to generate quantitative information and to check daily values, but the additional time and effort required to generate five triplicate points at each concentration level do not appear to be warranted by either the change in the values obtained or the precision of measurement observed in each case. Since the precision of measurement, as illustrated by the coefficient of variation, was less than 20 percent for all of the response factors for the compounds of interest, a mean value for the response factor was used in quantitative calculations and regression analysis was not used to generate a calibration curve.

SELECTION OF OTHER COMPOUNDS FOR QUANTITATION

Qualitative analysis was performed on five of the XAD-2® extracts in order to assess what additional compounds, other than the 3 targets, could be selected to study the effect of the distributive air volumes. The instrument was not calibrated for compounds other than the deuterated surrogates and the spiked target compounds (toluene, chlorobenzene, and 1,1,2,2-tetrachloroethane). Therefore, in order to obtain estimated quantities of the additional compounds, a relative response factor of 1 (relative to the analytical standard, d_{10}-phenanthrene) was assumed. The following equations were used for quantitation:

$$\text{Relative Response Factor} = \frac{A_{cpd}/ng_{cpd}}{A_{std}/ng_{std}}$$

where:

A_{cpd} = system response for the compound of interest

A_{std} = system response for the quantitation standard

ng_{cpd} = nanograms of compound of interest injected

ng_{std} = nanograms of standard injected

then:

$$ng_{cpd} = \frac{A_{cpd} \cdot ng_{std}}{A_{std} \cdot RRF}$$

The compounds selected to follow distributive air volumes were 4-methyl-2-pentanol, benzoic acid, benzoyl chloride, $C_{16}H_{33}CHO$, and diisooctyl phthalate. These compounds were selected because they were present in the XAD-2® extracts that were characterized and thus would possibly be present in varying amounts as a function of the volume of gas sampled. The results calculated for these compounds (assuming a relative response factor of 1) are shown in Tables F-4 and F-5. Using these compounds to illustrate variation in concentration as a function of volume of gas samples does not, in general, appear to be correct. Values for some of the compounds are observed to be higher in some of the blanks than in some of the samples, and the compounds do not exhibit even an approximate doubling in concentration when the volume of gas sampled doubles. A different choice of compounds may possibly better illustrate a change in concentration with change in sampled volume, but qualitative and quantitative characterization of more of the samples would be required. However, the change or lack of change in concentration with gas volume sampled with this particular selection of compounds does raise some interesting questions. Since these compounds are observed in XAD-2® extracts and extracts of media other than XAD-2® for actual samples and blanks, their presence may be due to artifact formation. Other than benzoyl chloride, which is usually present in low amounts, all of the other compounds are usually present in the extracts in substantial quantities. Granted that the quantitative values calculated are only estimates based on the assumption of a value of 1 for the relative response factor, a comparison of the relative sizes of the peaks in the chromatograms indicates that fairly extensive formation of these compounds must be occurring.

Qualitative analysis was performed with the aid of a computerized library search on the INCOS data system. Compounds observed are shown in Table F-6, which is presented in two parts. In Part 1, compounds which

TABLE F-4. COMPARISON OF RESULTS BY SAMPLE TYPE FOR PROBE RINSE, COIL RINSE, CONDENSATE/RINSE, AND IMPINGER/RINSE

Compound	Probe rinse			Coil rinse			Condensate and rinse		
	Blank-1	1-A*	1-B*	Blank-1	1-A*	1-B*	Blank-1	1-A*	1-B*
Surrogate compounds, % recovery									
d_8-1,4-dioxane	90	110	84	121	75	65	81	77	71
d_5-pyridine	100	118	86	118	80	64	74	71	58
d_8-toluene	92	109	91	70	72	61	84	41	39
d_5-chlorobenzene	97	116	92	118	80	67	90	68	53
d_5-phenol	106	115	87	112	86	71	97	87	75
d_8-nitrobenzene	113	140	97	110	94	70	137	106	90
d_8-naphthalene	105	131	101	78	97	82	114	89	84
$^{13}C_6$-pentachlorophenol	79	143	84	112	84	68	116	38	30
Target compounds, ng/uL									
toluene	3.1	9.2	7.0	3.0	3.6	3.2	4.0	NF#	NF
chlorobenzene	NF	NF	NF	NF	NF	NF	NF	NF	NF
1,1,2,2-tetrachloro-ethane	NF	NF	NF	NF	NF	NF	NF	NF	0.4
Other Compounds, ng/ul									
4-methyl-2-pentanol	NF	NF	NF	NF	NF	NF	4.6	3.6	NF
benzoic acid	4.9	7.0	NF	0.5	1.2	NF	NF	8.6	1.4
benzoyl chloride	NF	NF	NF	NF	NF	NF	NF	NF	NF
$C_{16}H_{33}CHO$	410	33.4	7.2	13.2	141	240	314	522	708
Diisooctyl phthalate	5.8	7.4	4.2	3.7	3.8	3.4	8.0	17.6	16.0
Sample Volume (dscf)	0	63.6	67.3	0	63.6	67.3	0	63.6	67.3

(continued)

TABLE F-4. (Continued)

	Impinger and rinse									
	Blank-1**	1-A*	1-B*	2-A*	2-B*	3-C	3-D	Mean	SD	% CV
Surrogate compounds, % Recovery										
d_8-1,4-dioxane	61	79	122	76	101	82	71	85.4	18.7	21.9
d_5-pyridine	67	77	114	85	98	82	77	85.6	18.9	22.1
d_8-toluene	41	69	91	40	50	45	27	63.9	24.5	38.3
d_5-chlorobenzene	49	76	105	58	64	57	44	77.1	23.6	30.6
d_5-phenol	76	78	109	84	105	87	78	90.8	14.5	15.9
d_8-nitrobenzene	86	102	156	98	138	118	103	109.9	22.9	20.9
d_8-naphthalene	72	91	122	94	106	94	75	95.9	16.7	17.4
$^{13}C_6$-pentachlorophenol	314	150	105	111	91	189	169	117.7	67.9	57.7
Target compounds, ng/ul										
Toluene	NF	NF	NF	NF	NF	NF	NF			
Chlorobenzene	NF	NF	NF	NF	NF	NF	NF			
1,1,2,2-tetrachloro-ethane	NF	NF	NF	NF	NF	NF	NF			
Other compounds, ng/ul										
4-methyl-2-pentanol	NF	2.4	NF	NF	NF	4.8	17.6			
benzoic acid	11.1	4.0	4.3	1.0	2.4	13.6	14.8			
Benzoyl chloride	NF	NF	NF	NF	NF	NF	NF			
$C_{16}H_{33}CHO$	27.2	54.4	16.7	12.8	31.7	18.4	82.2			
diisooctyl phthalate	2.9	3.6	3.8	4.4	9.4	6.6	116.6			
Sample Volume (dscf)	0.0	63.6	67.3	64.5	63.5	53.3	94.9			

* Field spike.

NF - not found.

** Mean of three replicates.

TABLE F-5. COMPARISON OF RESULTS BY SAMPLE TYPE FOR ALL XAD-2® TRAPS

		Run #1				Run #2				Run #3			
Compound	Blank-1	1-A*	1-B*	1-C	1-D	2-A*	2-B*	2-C	2-D	3-A	3-B	3-C	3-D
Surrogate compounds						% Recoveries							
d_8-1,4-dioxane	87	113	92	86	84	78	72	97	73	76	95	85	90
d_5-pyridine	92	103	85	91	87	78	74	91	74	60	51	16	58
d_8-toluene	81	104	89	92	81	77	75	87	65	68	92	79	80
d_5-chlorobenzene	89	116	91	96	89	79	82	102	75	79	92	90	95
d_5-phenol	101	119	102	105	95	92	86	115	89	84	107	94	101
d_5-nitrobenzene	107	150	141	115	108	102	120	148	103	110	128	128	134
d_8-naphthalene	102	136	120	113	98	98	98	127	101	102	122	106	111
$^{13}C_6$-pentachlorophenol	39	124	216	121	126	176	185	87	113	176	134	186	168
Target compounds, ng/uL													
toluene	NF#	10.1	17.4	2.4	2.0	16.0	20.4	NF	NF	2.0	7.3	2.6	7.0
chlorobenzene	0.1	23.8	28.0	26.1	22.6	34.7	60.1	20.3	20.8	23.6	53.9	24.8	51.0
1,1,2,2-tetrachloro-ethane	NF	1.8	2.0	NF	NF	1.4	1.2	NF	NF	NF	NF	NF	NF
Other compounds, ng/uL													
4-methyl-2-pentanol	3.6	83.0	135	74.2	53.8	282	143	150	137	248	291	318	270
benzoic acid	33.0	76.0	120	77.0	80.6	92.0	91.0	95.7	98.6	330	370	559	352
benzoyl chloride	56.4	16.9	35.6	19.2	17.0	36.0	31.5	21.1	22.8	22.2	21.5	21.6	24.8
$C_{16}H_{33}CHO$	40.8	241	6.2	12.1	5.6	2.0	11.0	12.7	16.6	26.0	16.3	15.8	23.8
diisooctyl phthalate	56.6	53.0	37.6	24.1	33.0	16.0	13.0	36.0	25.0	6.8	19.0	9.6	6.8
Sample Volume (dscf)	0.0	63.6	67.3	68.6	61.4	64.5	70.0	65.6	53.8	52.4	103	53.3	94.9

TABLE F-5. (Continued)

	Run #4					Run #5						
	Blank-3	4-A	4-B	4-C	4-D	4-D**	5-A	5-B	5-C	5-D	Mean	SD	% CV
Surrogate compounds, % recoveries													
d_8-1,4-dioxane	81	89	96	102	95	81	108	83	62	87	87.5	11.7	13.4
d_5-pyridine	79	90	97	103	93	79	107	83	70	80	80.0	20.0	25.0
d_8-toluene	77	84	95	96	87	75	99	78	60	83	82.8	10.8	13.1
d_5-chlorobenzene	82	96	105	105	100	83	115	87	64	89	91.3	12.4	13.6
d_5-phenol	86	101	115	116	102	98	112	93	82	100	99.8	10.8	10.8
d_5-nitrobenzene	95	112	140	143	114	119	137	118	105	112	121	16.1	13.3
d_8-naphthalene	94	109	127	135	114	120	128	125	100	100	112	13.1	11.7
$^{13}C_6$-pentachlorophenol	39	135	142	137	46	90	127	203	83	104	129	50.1	38.9
Target compounds, ng/ul													
toluene	NF	NF	2.2	NF	NF	NF	2.0	2.6	NF	2.4			
Chlorobenzene	NF	20.0	37.6	21.1	2.8	16.6	26.4	33.0	15.0	30.8			
1,1,2,2-tetrachloro-ethane	NF	NF	NF	NF	NF	NF	NF	NF	NF	NF			
Other compounds, ng/ul													
4-methyl-2-pentanol	NF	61.8	180	35.2	2.4	127	150	124	129	136			
benzoic acid	31.0	106	73.6	93.8	42.0	86.2	92.6	89.2	60.9	61.9			
benzoyl chloride	37.6	23.2	15.4	22.2	22.2	16.1	20.8	18.6	13.3	13.0			
$C_{16}H_{33}CHO$	11.2	33.0	28.2	18.6	32.6	94.0	55.6	29.0	48.0	48.4			
diisooctyl phthalate	7.2	37.2	24.8	49.2	28.4	83.0	17.4	23.4	391	242			
Sample Volume (dscf)	0.0	35.1	61.0	35.6		60.2[c]	32.0	60.5	32.2	58.4			

* Dynamic field spikes

NF - not found.

** Two XAD-2 traps used during this run.

TABLE F-6. QUALITATIVE ANALYSIS

Part 1. Compounds Common to All Samples Characterized

Compound	Radian #8261 Run 1-A, XAD Scan # (Confidence Level)	Radian #8285 Blank, XAD	Radian #8267 Run 1-B, XAD	Radian #8339 Run 3-D, XAD	Radian #8327 Run 3-C, XAD
4-methyl-2-pentanol	344 (3)	326 (3)	330 (3)	324 (3)	338 (3)
ethyl carbamate	451 (2)	440 (2)	443 (2)	437 (2)	—
ethylbenzene	502 (3)	493 (3)	495 (3)	492 (3)	499 (3)
m-,p-xylene	513 (3)	504 (3)	507 (3)	504 (3)	510 (3)
o-xylene	547 (3)	539 (3)	542 (3)	539 (3)	544 (3)
benzaldehyde	635 (3)	630 (3)	633 (3)	631 (3)	634 (3)
hexanoic acid	643 (2)	639 (2)	641 (2)	640 (2)	645 (2)
phenol	653 (3)	649 (3)	651 (3)	649 (3)	652 (3)
dichlorobenzenes	694 (3), 702 (3), 730 (3)	—	692 (3), 728 (3)	698 (3), 727 (3)	700 (3), 728 (3)
acetophenone	763 (3)	760 (3)	762 (3)	761 (3)	762 (3)
benzoic acid	860 (3)	860 (3)	867 (3)	869 (3)	874 (3)
ethylbenzaldehydes	870 (3), 887 (3)	868 (3), 885 (3)	870 (3), 887 (3)	886 (3)	886 (3)
benzoyl chloride	983 (3)	982 (3)	984 (3)	983 (3)	983 (3)
ethylbenzoic acid	1038 (3), 1049 (3)	1039 (3), 1050 (3)	1041 (3), 1053 (3)	1040 (3), 1051 (3)	1040 (3), 1051 (3)
hexadecane	1251 (2)	—	1252 (3)	1251 (3)	1250 (3)
heptadecane	—	1327 (2)	1328 (3)	1327 (3)	1327 (3)
tetradecanoic acid	1368 (3)	1368 (3)	1369 (3)	—	—
phenanthrene	—	—	1424 (2)	1423 (3)	1422 (3)
diisooctyl phthalate	1984 (3)	1986 (3)	1987 (3)	1985 (3)	1984 (3)
$C_{16}H_{33}CHO$	1579 (2)	1578 (2)	1580 (2)	1583 (2)	1581 (2)

(continued)

TABLE F-6. (continued)

Part 2. Other Compounds Identified

Radian #0261 Run 1-A, ZAD	Radian #0285 Blank, ZAD	Radian #0267 Run 1-B, ZAD
p-chloroaniline (833, 3)	i-butyl acetate (419, 1)	chloropropene (373, 2)
nonanoic acid (955, 2)	methylstyrenes (675, 3; 679, 3)	alkoxy alkanol (423, 1)
3-(1,1-dimethylethyl) phenol (990, 3)	heptanoic acid (752, 1)	5-methyl-2-hexanone (488, 1)
$C_{13}H_{28}$ (994, 2)	methyl benzoate (792, 2)	2-butoxyethanol (556, 1)
tetradecane (1084, 2)	nonanal (797, 2)	methylstyrenes (677, 3; 681, 3)
dodecanal (1095, 3)	p-chloroaniline (831, 1)	trimethylcyclohexanone (731, 1)
$C_{12}H_{24}$ (1149, 3)	dodecanal (904, 3)	heptanoic acid (755, 1)
dodecanoic acid (1215, 2)	nonanoic acid (954, 2)	$C_{11}H_{24}$ (794, 2)
N-phenylaniline (1286, 3)	dodecanoic acid (1214, 3)	methyl 2,4-hexadienoate (797, 2)
$C_{14}H_{28}$ (1311, 3)	N-phenylaniline (1281, 3)	methyl octanoate (819, 2)
2-(dodecyloxy) ethanol (1344, 1)	pentadecanoic acid (1439, 2)	p-chloroaniline (833, 3)
3-hexadecene (1458, 3)	1-hexadecanol (1457, 3)	2,3-dichlorophenol (875, 3)
hexadecanoic acid (1508, 2)	nonadecane (1469, 2)	2-(2-ethoxyethoxy) ethanol acetate (880, 1)
phthalate ester (1521, 3)	9-hexadecenoic acid (1496, 3)	naphthalene (899, 3)
2-tetradecanol (1537, 2)	hexadecanoic acid (1508, 2)	3-phenyl-2-propenal (908, 2)
3-octadecene (1591, 3)	phthalate ester (1521, 3)	dichlorophenol (912, 3)
$C_{18}H_{36}$ (1664, 2)	5-octadecene (1591, 3)	dimethylbenzaldehyde (935, 1)
2-heptadecanol (1713, 1)	$C_{16}H_{32}$ (1624, 3)	dichloroaniline (952, 3)
phthalate ester (1975, 3)	dihexyl hexanedioate (1634, 1)	nonanoic acid (957, 2)
phthalate ester (2277, 3)	4-(dimethylamino) benzoic acid (1728, 1)	1-(4-ethylphenyl) ethanone (970, 3; 990, 2)
$C_{20}H_{36}O$ (2473, 1)	2-tridecanol (1771, 1)	$C_{13}H_{28}$ (995, 3)
	dioctyl hexanedioate (1815, 3)	methylnaphthalenes (1009, 3; 1027, 3)
	triphenyl phosphate (1849, 3)	decanoic acid (1048, 1)
	$C_{18}H_{38}O$, alcohol (1872, 1)	trichlorophenol (1058, 2)
	fatty acid methyl ester (1888, 1)	tetradecane (1086, 3)
	unknown (1919)	tetrachlorobenzene (1089, 1)
	phthalate ester (2277, 3)	trichlorophenol (1089, 1)
	9-octadecenamide (2358, 1)	pentadecane (1171, 2)
	$C_{30}H_{50}$ (2473, 2)	methyl methylundecanoate (1191, 2)
		(1-butylhexyl)benzene (1209, 3)
		(1-propylhepty1)benzene (1216, 2)
		(1-ethyloctyl)benzene (1233, 3)
		(1-methylnonyl)benzene (1262, 3)
		N-phenylaniline (1287, 3)
		(1-propyloctyl)benzene (1295, 3)
		$C_{19}H_{40}$ (1334, 2)
		(1-methyldecyl)benzene (1340, 3)
		methyl tetradecanoate (1347, 3)
		(1-pentylhepty1)benzene (1357, 3)
		(1-butyloctyl)benzene (1361, 3)
		(1-ethyldecyl)benzene (1388, 3)
		$C_{15}H_{32}$ (1409, 3)
		(1-methylundecyl)benzene (1415, 3)
		(1-butylnonyl)benzene (1433, 1)
		(1-propyldecyl)benzene (1442, 1)
		1-phenyl-1,2-propanedione (1467, 2)
		nonadecane (1471, 2)
		dibutyl propanedioate (1487, 1)
		methyl methylundecanoate (1489, 1)
		5-octadecene (1497, 2)
		hexadecanoic acid (1509, 2)
		butyl octyl phthalate (1522, 2)
		eicosane (1536, 1)
		i-propyl hexadecanoate (1552, 3)
		$C_{16}H_{30}$ (1580, 3)
		$C_{20}H_{40}$ (1593, 2)
		$C_{17}H_{28}$ (1600, 1)
		octadecanoic acid (1636, 2)
		dioctyl hexanedioate (1816, 3)
		dihexyl nonanedioate (1873, 1)
		$C_{16}H_{25}N$ (2474, 1)

(continued)

Reproduced from best available copy.

TABLE F-6. (continued)

Part 1. Other Compounds Identified (continued)

Radian #8339 Run 3-D, XAD	Radian #8327 Run 3-C, XAD
dibromomethane (246, 3)	dibromomethane (230, 3)
1,4-dioxane (257, 3)	1,4-dioxane (241, 3)
4,4-dimethyl-2-pentanone (375, 1)	chloropropene (368, 2)
1-chloro-1-propene (380, 3)	furfural (445, 1)
dibromochloromethane (396, 3)	bromoform (526, 3)
hexanal (404, 2)	3-bromo-1-propyne (560, 2)
butyl acetate (428, 1)	bromobenzene (593, 3)
Cl_2 compound (441, 1)	C_3-alkylbenzene, methylstyrene (675)
furfural (454, 1)	alkoxy alkanol (771)
3,3-dimethyl-2-hexanone (460, 1)	Br_2 compound (919)
bromoform (532, 3)	nonanoic acid (956, 2)
2-heptanone (537, 2)	ethylacetophenone (970, 3)
heptanal (553, 2)	C_2-alkylacetophenone (990, 2)
$C_3H_3Br_2F$ (tentative) (565)	$C_{13}H_{28}$ (994, 3)
bromobenzene (597, 3)	methylnaphthalenes (1009, 2; 1026, 2)
methylbenzaldehyde (677, 2)	bromodichlorophenol (1142, 2)
methylstyrene (677, 3)	$C_{15}H_{32}$ (1170, 2)
octanal (683, 3)	C_2-alkylnaphthalene (1195, 3)
Br_2 compound (695)	Cl_2Br compound (1195)
C_8H_{14} (705, 1)	dodecanoic acid (1215, 2)
2-methyl-1-butanol acetate (756, 2)	Cl_3Br compound (1223)
alkoxy alkanol (771)	Cl_3Br compound (1228)
unknown (785)	Cl_3Br compound (1282)
unsaturated C_4-alkylbenzene (793, 2)	Cl_3Br compound (1309)
brominated compound (832)	tribromophenol (1309, 3)
naphthalene (898, 3)	$C_{19}H_{40}$ (1332, 3)
Br_2 compound (919)	Br_2 compound (1345)
nonanoic acid (956, 3)	tribromoaniline (1362, 2)
ethylacetophenone (969, 3)	hexadecanoic acid (1508, 2)
$C_{13}H_{28}$ (993, 3)	phthalates (1521, 2277)
methylnaphthalenes (1008, 3; 1026, 2)	Cl_2Br compound (1536)
1-(1,1-dimethylethyl)-4-ethoxybenzene (1075, 3)	
Br compound (1140)	
$C_{15}H_{32}$ (1169, 3)	
Br_2 compound (1222)	
$ClBr_2$ compound (1228)	
$ClBr_2$ compound (1282)	
tribromophenol (1308, 3)	
Br compound (1323)	
Br_2 compound (1345)	
tribromoaniline (1362, 3)	
hexadecanoic acid (1507, 3)	
phthalates (1520, 2140, 2276)	
2,3-dibromothieno[3,2-C] pyridine (1548, 2)	
nonadecane (1810, 3)	
$C_{21}H_{44}$ (1910, 1)	
$C_{21}H_{44}$ (2031, 1)	

were common to all the XAD-2® extracts characterized are listed together. The identification of 4-methyl-2-pentanol was confirmed by injection of an authentic standard. This compound has frequently been observed in XAD-2® extracts and may be an artifact of this process. Another compound of interest observed in most of the extracts analyzed in this study is listed in Table F-6 as $C_{16}H_{33}CHO$. This compound is a major constituent of all of the chromatograms and is not definitively identified by computerized library search. A mass spectrum of this compound is shown in Figure F-1. An inspection of the spectrum shows peaks characteristic of the fragmentation pattern exhibited by aliphatic aldehydes. A molecular ion at mass 254 suggests that the compound is an aliphatic (as opposed to cyclic or unsaturated) aldehyde, with a peak at m/z 210 being characteristic of a mass spectrometric rearrangement process which occurs in this type of compound and indicates the presence of hydrogen in the position gamma to the carbonyl carbon. A further interesting note on the presence of this compound is its occurrence in all of the media studied, not just XAD-2® extracts. This observation suggests that the compound may be present for reasons other than XAD-2® artifact formation.

The two samples from Run 3 showed extensive presence of brominated compounds. The presence of dibromomethane was anticipated, since this compound was spiked into the waste during Run 3. However, bromoform, bromobenzene, dibromochloromethane, tribromophenol, tribromoaniline, and other compounds with both chlorine and bromine, which could not be identified, were also observed in one or both of the samples. Hexachlorocyclopentadiene was spiked during Runs 4 and 5, but no extensive characterization of compounds was performed for these samples. Based on the observations of Run 3 samples (dibromomethane feed), substantial numbers of variously chlorinated compounds would be expected if series 4 and 5 samples were characterized.

Extracted ion current profiles have been plotted for various samples, using ions characteristic of different compound series. Figure F-2 shows the extracted ion current profile obtained for mass 57, characteristic of saturated hydrocarbons, in Sample 8376, an extract of XAD-2® from Run 5-B. Figure F-3 shows the extracted ion current profile of mass 91, characteristic of aromatic systems, for the same sample.

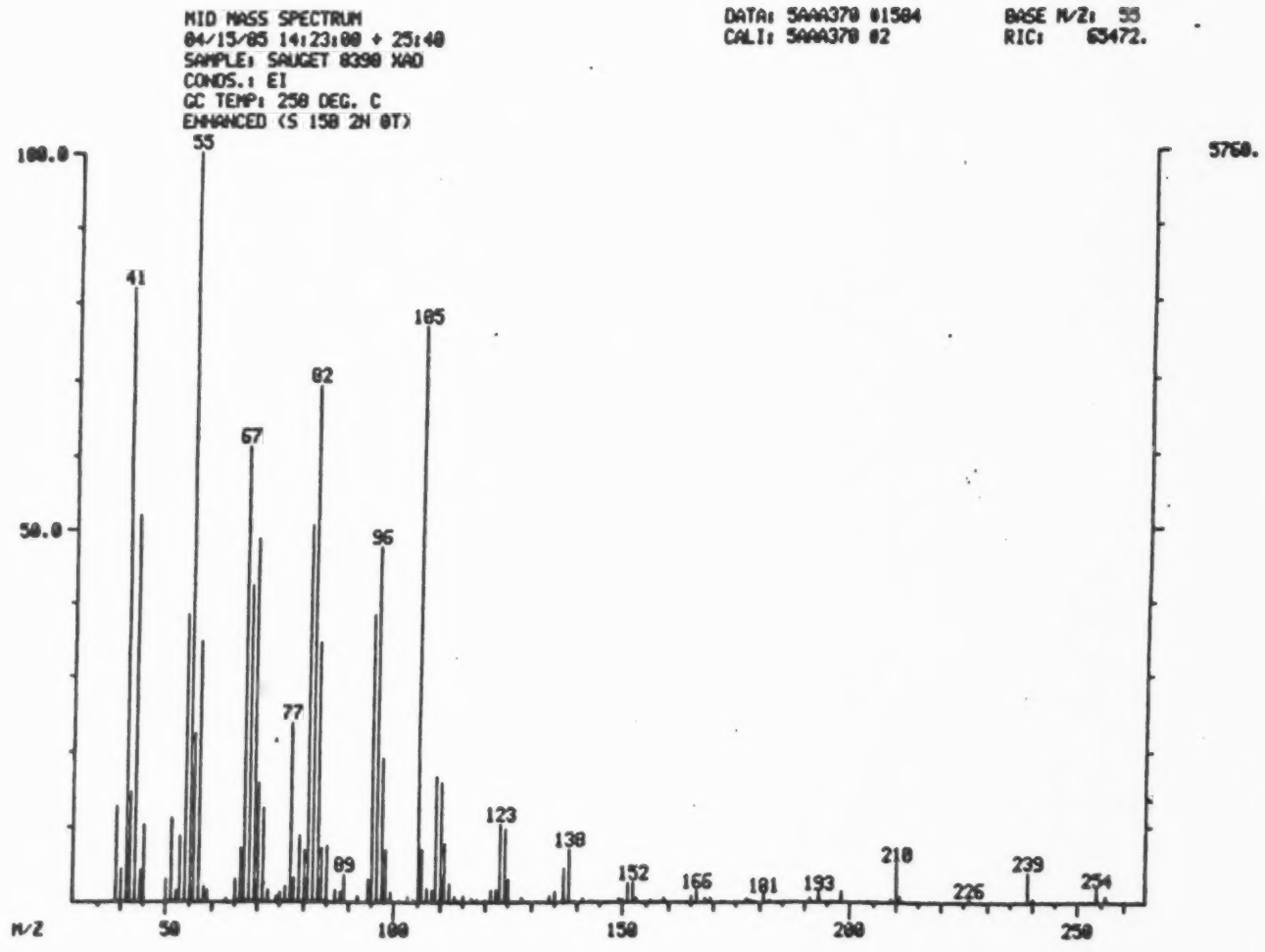


Figure F-1. Mass spectrum of the compound identified as $C_{16}H_{33}CHO$, present in all extracts.

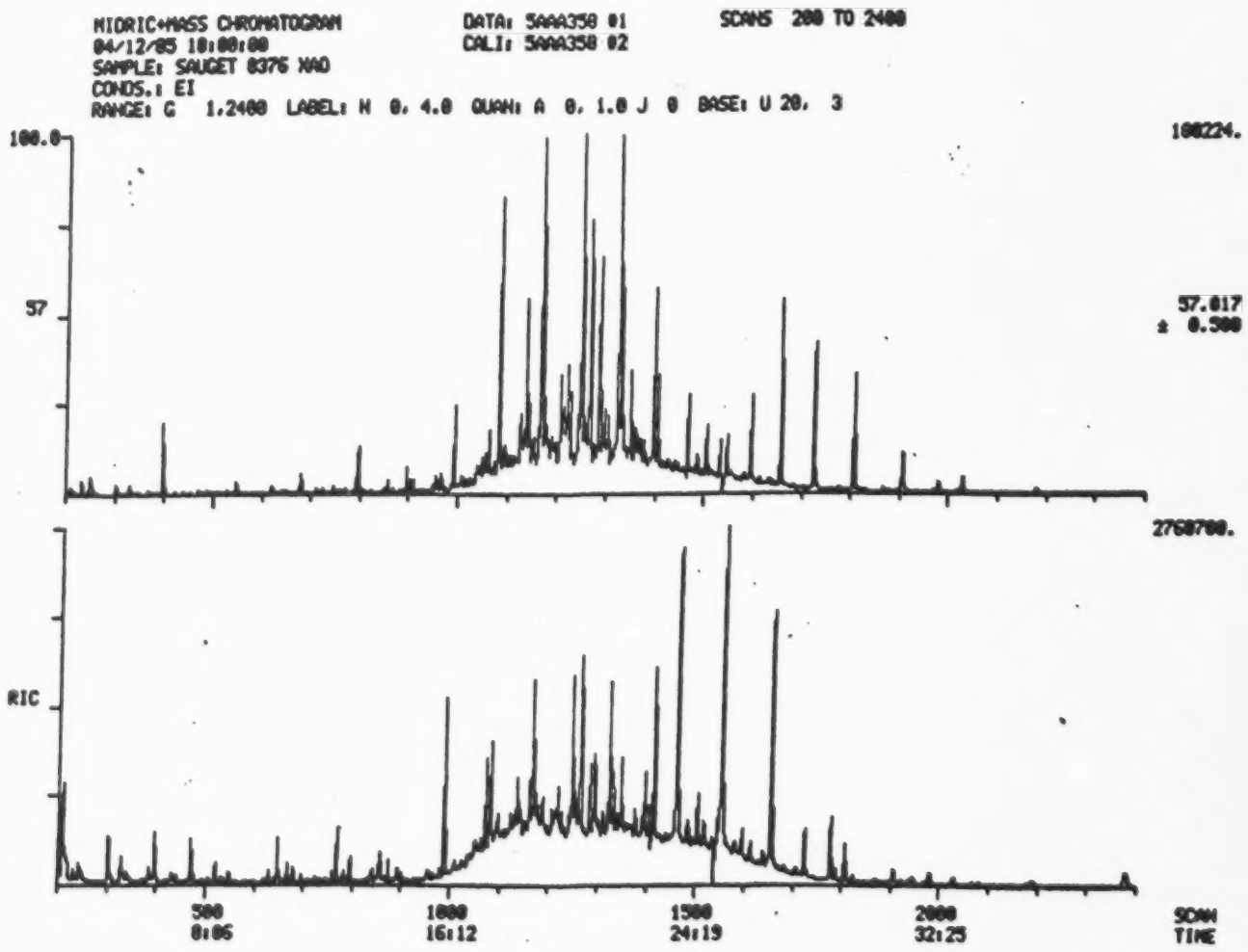


Figure F-2. Extracted ion current profile of mass 57, characteristic of saturated hydrocarbons, for Sample 8376, an extract of XAD-2® from Run 5-B.

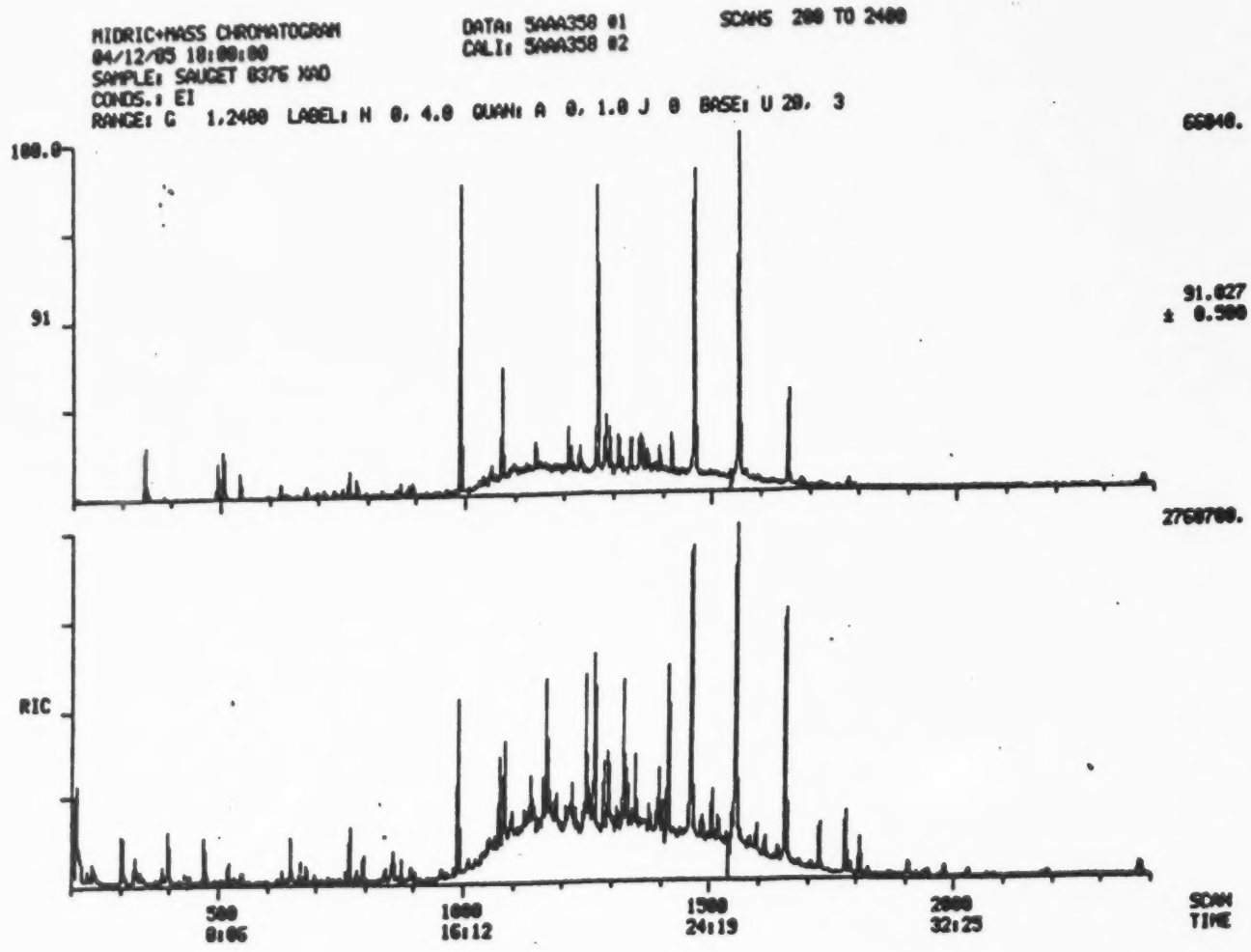


Figure F-3. Extracted ion current profile of mass 91, characteristic of aromatic systems, for Sample 8376, XAD-2® extract, Run 5-B.

Figure F-4 shows extracted ion current profiles of masses 74 and 87, characteristic of methyl esters of aliphatic carboxylic acids for the same sample. Figure F-5 shows extracted ion current profiles of masses 60 and 73, characteristic of aliphatic carboxylic acids, for the XAD-2® extract of Sample 8267, from Run 1-B. Figure F-6 shows the extracted ion current profile of mass 149, characteristic of phthalate esters, for the XAD-2® extract of Sample 8267, from Run 1-B. These figures show that saturated hydrocarbons are extensively present, with the regular n-alkane series ranging from approximately C_{14}-C_{18}. Earlier-eluting hydrocarbons have many branched species interspersed with the n-alkanes. Aromatic systems, starting with toluene and continuing (for some samples) through C_5-C_{12} alkylbenzenes, are also observed in the samples. There are a few methyl esters, but for the most part, this is not a class of compounds which is present either in large numbers or in large amounts. Some of the samples show the presence of carboxylic acids, which have been cited in the literature as possible artifacts of XAD-2® extraction with polar solvents. In the present situation, no polar solvents such as diethyl ether were used to extract the XAD-2®; extraction was performed with methylene chloride. Also, no non-XAD-2® extracts were characterized to determine if the carboxylic acids were also present when no XAD-2® is extracted. The phthalate esters are plasticizers, and are virtually ubiquitous as contaminants. These peaks may be observed as a result of use of, and subsequent concentration of, organic solvent or as the result of contact of any part of the sample system or solvent with plastic containers or tubing. Presence of phthalates as a function of the use and concentration of methylene chloride is very highly probable, since these phthalate esters are observed both in XAD-2® extracts and in all other samples studied as well.

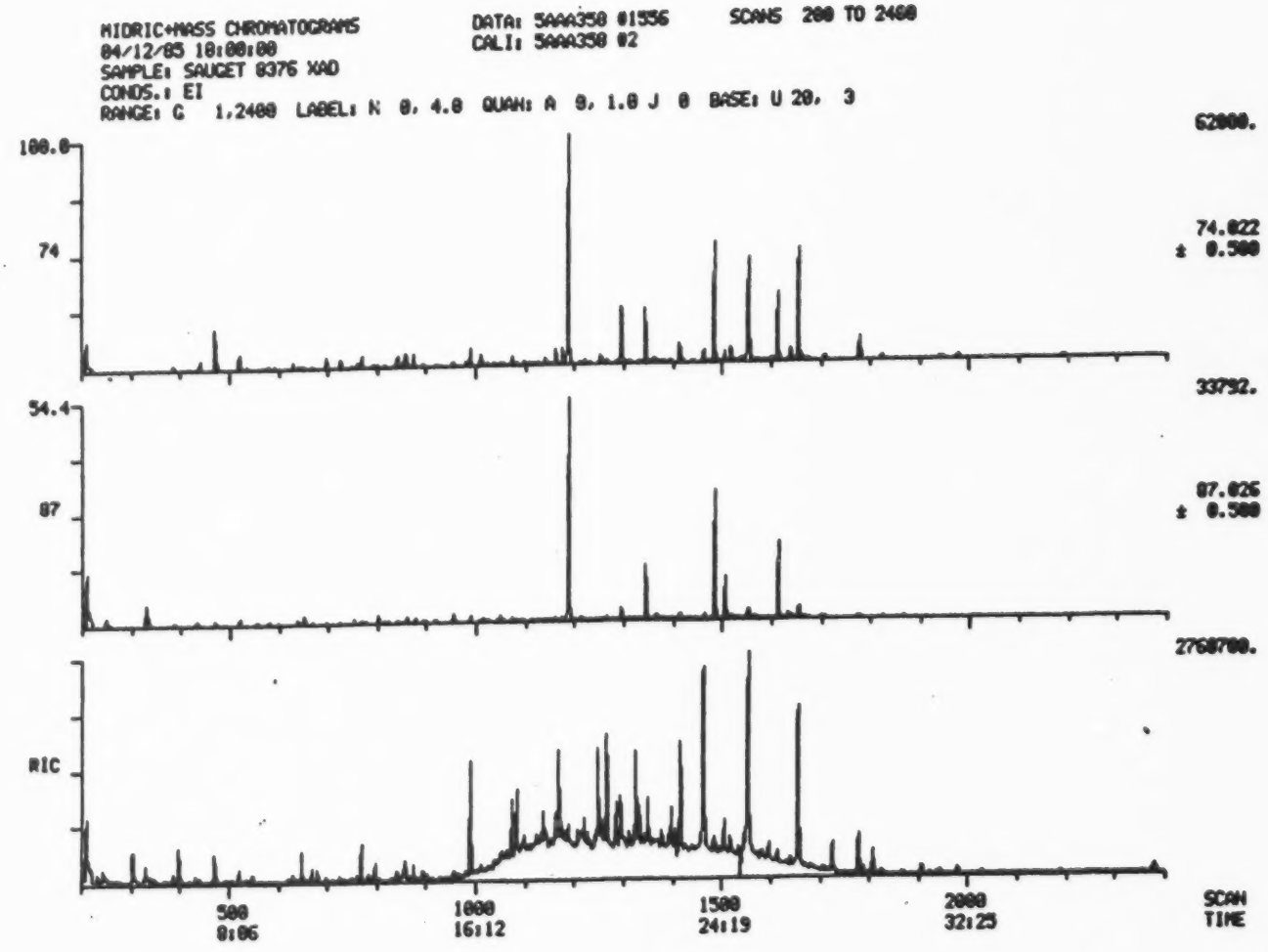


Figure F-4. Extracted ion current profile of mass 149, characteristic of phthalate esters (plasticizers) for the XAD-2® extract of Sample 8267, Run 1-B.

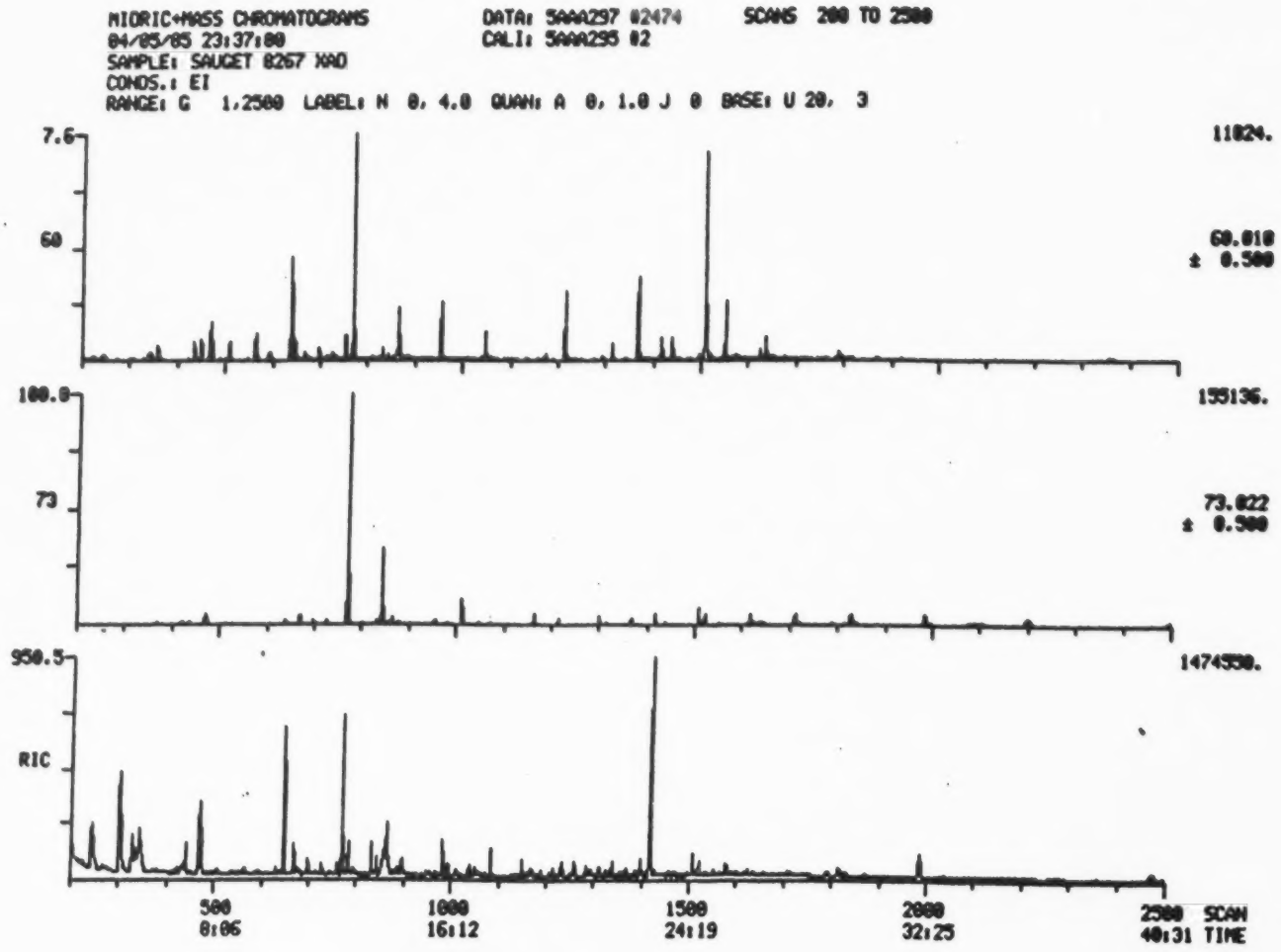


Figure F-5. Extracted ion current profile of masses 74 and 87, characteristic of methyl esters of aliphatic carboxylic acids, for the XAD-2® extract of Sample 8376, Run 5-B.

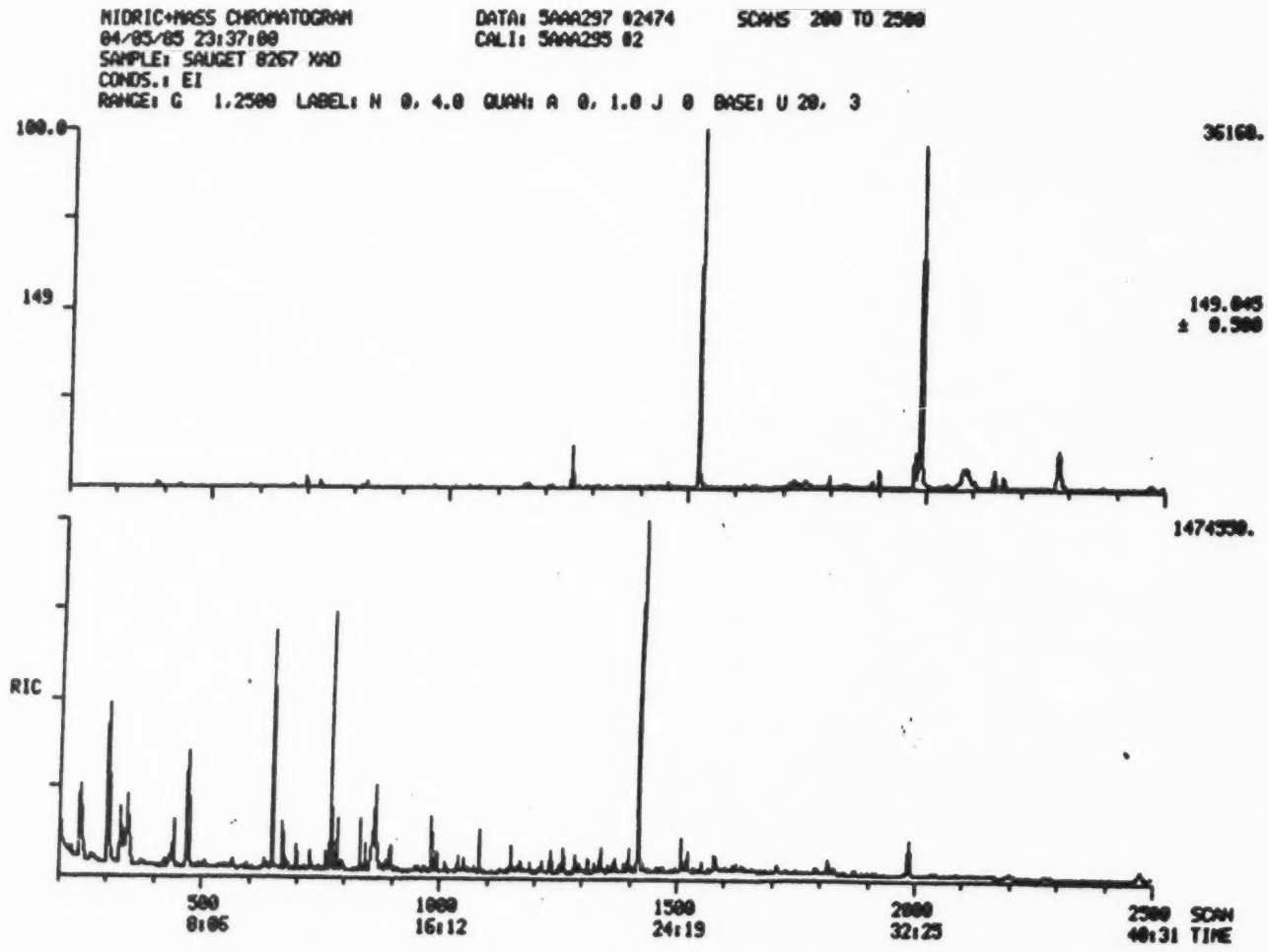


Figure F-6. Extracted ion current profile of masses 60 and 73, characteristic of aliphatic carboxylic acids, for the XAD-2® extract of Sample 8267, Run 1-B.

APPENDIX G
QUALITY ASSURANCE/QUALITY CONTROL

The quality assurance (QA) activities used for the field test evaluation of the Semi-VOST sampling and analysis methodology are detailed in the Quality Assurance Project Plan for that field test.[1] The QA project plan was designed according to the guidelines proposed in the EPA draft document "Guidelines and Specifications for Preparing Quality Assurance Project Plans," QAMS-005/80.

In this appendix, the following quality control/quality assurance (QA/QC) data are presented: (1) a summary of field quality control procedures; and (2) data from the analyses of check samples prepared by the Research Triangle Institute. Representative examples are presented for: (1) control charts for the daily analyses of calibration standards to monitor stability of response factors used to calculate recoveries of surrogates and quantities of compounds; (2) daily tuning data from the gas chromatograph/mass spectrometer/data system for decafluorotriphenylphosphine, the compound used as a tuning standard; and (3) data from the column performance standard, analyzed weekly to monitor possible deterioration of the chromatographic column.

QUALITY CONTROL OF FIELD ACTIVITIES

Calibrations of Field Equipment

The consoles, thermocouples, temperature gauges, and probe nozzles were calibrated as described in Section 3.4.2 of EPA document 600/4-77-027b, Quality Assurance Handbook for Air Pollution Measurement Systems. The type S pitot tube assembly was calibrated using the procedure in Section 3.1.2 of EPA Reference Method 2.

---

[1] Quality Assurance Project Plan: Field Test Evaluation of the Semi-VOST Sampling and Analysis Methodology at the Trade Waste Incineration Facility; Sauget, Illinois; Radian Corporation, December 10, 1984.

The spiking system was designed by Radian Corporation and was calibrated by following the procedure outlined in the QA/QC plan. In addition to the calibration and check out of the dynamic spiking system in the laboratory prior to the field test, the procedures for checking the system output both for concentration of the VOC and flow from the mass flow controllers as depicted in Figure 2 of the experiment were carried out in the field just prior to testing and immediately following testing.

Quality Objectives

In order to ensure the completeness of the field data, several quality objectives were put in place. They included leak checks, consistency of clean-up procedures, monitoring the flow, temperature and vacuum gauges throughout the testing period, noting abnormalities during testing, and complete documentation of data.

One of the criteria for sampling for each run was the need to obtain good (<.02 CFM) leak checks on each of the four trains that were to be run simultaneously. In all cases, this leak check was satisfactory both before and after testing. In one case (Run 3), the filters plugged on the two trains which were conducting the 4-hour run. Satisfactory leak checks were performed before disassembly of the plugged trains and prior to conducting tesing with the new filters.

To ensure consistency between the trains, one person was assigned to clean up, recover, and re-assemble the glassware. This protocol served to eliminate the propogation of multiple operator variance for the method precision experiments.

The isokinicity was not within the 90 to 110 percent range for all runs. Wherever possible, this criterion was followed. However, in some runs, maintaining the flow rate of 0.5 CFM through the train was required for the experiment. Since the flow through the stack was variable, only one of these requirements could be met at times.

Other Effects on Sampling Quality

During testing, two factors occurred that were not anticipated from the pre-test visits. The first of these factors was the extremely cold weather conditions that prevailed during the testing period. An attempt

to test at the facility had been made 2 weeks earlier and had been aborted because of low temperatures and high wind conditions (wind chill factors of -77°F). At that time, it was determined that the sampling locations should be enclosed with a wind protective shell. Plant personnel enclosed the test scaffolding with PVC film tacked on a wooden frame. During testing, temperatures inside the test location ranged from 30 to 50°F while the outside temperatures ranged from 0 to 25°F with wind chills as low as -22°F. With this precaution taken, the impinger trains and dynamic spiking system were rarely subjected to freezing temperatures during sampling. While these temperatures may have had an effect on the sampling system, it would not be an abnormal effect for winter sampling.

The second factor which became evident during the testing period was the variability of the process feed. During the testing periods, solid waste of variable contents were fed to the incinerator every 5 to 10 minutes. This caused a minor upset period during the time of the feed. There should be no effect on the precision of measurements within a quad run conducted over the same time period but there could be effects between runs conducted over differing time periods.

ANALYSIS OF CHECK SAMPLES SUPPLIED BY THE RESEARCH TRIANGLE INSTITUTE

The Research Triangle Institute prepared two check samples for analysis by the Radian Research Triangle Park Laboratories. These samples consisted of two XAD-2® modules which had been spiked with known quantities of toluene, chlorobenzene, and 1,1,2,2-tetrachloroethane. Four blanks were also supplied with these check samples. Two of the blanks were reserved in the laboratory and two were sent to the field as "trip blanks." The results of the analyses are shown in Table G-1. The spiked compounds were not observed in the blank samples. With the exception of pentachlorophenol, surrogate recoveries were consistent and reasonably near 100 percent.

Table G-2 shows the comparison of the observed values with the "expected" levels of the three compounds spiked onto the XAD-2® by the Research Triangle Institute. The precision of the spiking methodology employed by RTI is estimated as 20.6, 33.8, and 10.5 percent relative

for toluene, chlorobenzene, and 1,1,2,2-tetrachloroethane, respectively. Recoveries of approximately 80 percent were obtained for the deuterated surrogates which Radian added to samples M-1 and P-1. These values are reasonable for both toluene and chlorobenzene following extraction and K-D concentration. The surrogate-corrected recovery efficiency for toluene was 87 and 89 percent for samples M-1 and P-1, respectively. Corresponding recoveries for chlorobenzene were 88 and 90 percent. All values were within the estimated acceptance ranges for RTI's expected loadings. Therefore, no bias was introduced during the analyses of the RTI spiked samples in the Radian Laboratory.

DAILY CALIBRATION OF THE GC/MS SYSTEM

An initial calibration of the GC/MS system was performed using triplicate injections at each of five concentration levels to generate a response factor data base. The generation of this data base is discussed in Appendix F. A comparison of the 15-point data base with a 5-point data base (one injection at each of the five concentration levels) is also discussed in Appendix F. The protocol for the analysis of field samples required the analysis of two calibration standards each day, one at the beginning of the day and one at the end of the day. Two presentations of the results of these daily analyses are made - control charts for the individual compounds and a tabular summary of the values. Figures G-1 through G-23 are the control charts. The mean response factor from the 15-point data base is shown as the mean value in the control charts. Around that mean, the standard deviation of the values in the data base is shown as 1 σ, 2 σ, and 3 σ. Nearly all of the points obtained in the daily analyses of calibration samples are within the 3 σ range of the control charts. Table G-3 presents the same information in tabular form. The value of the response factor calculated for each ion of each compound is shown with the date for the analysis. The mean of this set of daily values is calculated, as is the standard deviation and the percent coefficient of variation. The mean of the set of daily values is then compared to the mean of the same response factor from the 15-point data base, and a relative percent difference is calculated. The values differ by 15 percent or less, showing excellent

stability for the analytical instrument and entirely acceptable reproducibility of values for the response factors over the entire period of the analytical determinations.

DAILY TUNING DATA FOR THE GC/MS SYSTEM

The compound decafluorotriphenylphosphine (DFTPP) was used as the daily tuning standard for the mass spectrometer. The criteria for acceptability of the tune of the mass spectrometer are shown in Table 4-2 of Appendix A. No analysis was performed until the instrument had satisfied tuning criteria every day. The data obtained for the daily analyses of DFTPP are shown in three forms. The first entry for every day is a chart showing the ions specified in the table of criteria, with a comparison of the values obtained with the specified values. The second set of information shows a plotted mass spectrum obtained daily from the analysis of DFTPP, and the third set of data includes a list of the masses and intensities obtained for this compound. An inspection of the values obtained for analysis of DFTPP also illustrates the excellent stability of the mass spectrometer during this study.

ANALYSIS OF THE COLUMN PERFORMANCE SOLUTION

The column performance solution consists of a mixture of compounds which are intended to test the condition of the chromatographic column in order to decide whether column maintenance should be performed on a given chromatographic column. Critical parameters are resolution, separation number, and peak asymmetry. The calculations and values obtained are described below.

Column Performance Data

Components of the column performance standard:

- octanone
- decane
- 1-octanol
- undecane
- 2,6-dimethylphenol
- 2,6-dimethylaniline

- naphthalene
- dodecane
- tridecane

Resolution (octanone, decane):

$$R = \frac{2\ (\text{distance between peak tops})}{(\text{width of peak 1} + \text{width of peak 2})} \quad \text{at base}$$

Separation number (undecane, tridecane)

$$SN = \frac{(\text{distance between peak tops})}{(\text{width of peak 1} + \text{width of peak 2})} \quad \text{at half-height}$$

Percent peak asymmetry factor (2,6-dimethylphenol (2,6-DMP), 2,6-methylaniline (2,6-DMA), 1-octanol)

$$\text{Percent PAF} = \frac{(\text{width of back half of peak})}{(\text{width of front half of peak})} \times 100 \text{ at 10\% height}$$

Values calculated:

	4/01/84	4/09/85	4/15/85
R	1.7	2.0	2.1
SN	35	41	47
Percent PAF			
2,6-DMP	50	91	100
2,6-DMA	67	71	70
1-octanol	64	73	85

TABLE G-1. ANALYSIS RESULTS OF RTI XAD-2® SAMPLES

Compounds	Lab blank 1	Lab blank XAD	Travel blank XAD	Travel blank XAD	Spike P-1	Spike M-1	Mean	SD	% CV
Surrogate Compounds % Recoveries									
d_8-1,4-dioxane	75	79	80	103	82	83	83.7	9.9	11.8
d_5-pyridine	84	83	78	105	85	88	87.2	9.3	10.7
d_8-toluene	75	71	75	92	79	79	78.5	7.3	9.2
d_5-chlorobenzene	75	78	84	111	85	86	86.5	12.8	14.7
d_5-phenol	92	83	95	115	100	103	98.0	10.8	11.1
d_5-nitrobenzene	91	91	103	137	111	120	108.8	17.8	16.4
d_8-naphthalene	91	85	111	121	105	104	102.8	13.1	12.8
$^{13}C_6$-pentachlorophenol	45	113	10	150	69	37	70.7	52.1	73.7
Target Compounds, ng/vL									
Toluene	NF*	0.05	0.4	1.0	24.2	24.0			
Chlorobenzene	NF	NF	NF	NF	25.2	25.2			
1,1,2,2-tetrachloroethane	NF	NF	NF	NF	24.8	24.6			
Other Compounds ng/vL									
4-methyl-2-pentanol	6.1	59.6	5.2	19.2	5.0	5.2			
Benzoic acid	23.7	45.8	44.4	77.4	49.2	45.6			
Benzoyl chloride	58.3	17.0	57.6	51.6	39.4	55.2			
$C_{16}H_{33}CHO$	16.3	94.8	286.6	42.6	271.2	191.4			
Diisooctyl phthalate	88.6	55.6	67.6	184.2	30.4	26.8			

* NF = not found.

TABLE G-2. COMPARISON OF ANALYTICAL RESULTS FOR XAD-2® SPIKED BY RTI

Sample	Compound	Expected loading* (µg)	Measured loading (µg)	Recovery efficiency (percent)	Corrected loading† (µg)	Corrected recovery efficiency (percent)
M-1	Toluene	175±36.1	120	69	152	87
	Chlorobenzene	168±56.8	126	75	147	88
	1,1,2,2-tetra-chloroethane	162±17.0	123	76	-§	-§
P-1	Toluene	172±35.4	121	70	153	89
	Chlorobenzene	165±55.8	126	76	148	90
	1,1,2,2-tetra-chloroethane	159±16.7	124	78	-§	-§

* Expected RTI loading ± uncertainty (µg) introduced by loading precision.

† Measured loading as corrected by the recovery efficiency of the deuterated internal standard.

§ No deuterated internal standard available.

TABLE G-3. DAILY CALIBRATION SAMPLES

Compound	Ion	4/8	4/9	4/9	4/10	4/10	4/11	4/11	4/12	4/13	4/15
$^{d}_{10}$-phenanthrene	160	113889	123365	124011	135753	143404	131496	163875	132353	138661	141258
$^{d}_{8}$-1,4-dioxane	62	0.488	0.474	0.484	0.494	0.442	0.485	0.334	0.498	0.431	0.498
	96	1.368	1.441	1.361	1.443	1.277	1.429	1.070	1.487	1.342	1.526
$^{d}_{5}$-pyridine	52	1.441	1.383	1.358	1.239	1.160	1.250	1.172	1.287	1.194	1.147
$^{d}_{8}$-toluene	54	0.952	0.994	0.956	0.964	0.841	0.974	0.887	1.019	0.867	0.934
	70	1.077	1.120	1.110	1.075	0.947	1.062	1.035	1.141	1.041	1.104
$^{d}_{5}$-chlorobenzene	54	1.965	1.985	1.983	2.024	1.805	1.987	1.845	2.123	1.902	1.941
	117	4.509	4.661	4.588	4.601	4.110	4.494	5.094	4.861	4.591	4.792
	119	1.468	1.502	1.466	1.480	1.332	1.448	1.638	1.580	1.459	1.534
$^{d}_{5}$-phenol	71	1.897	1.719	1.883	1.731	1.560	1.580	1.527	1.729	1.691	1.457
$^{d}_{5}$-nitrobenzene	98	0.432	0.369	0.433	0.302	0.334	0.314	0.400	0.337	0.356	0.306
	128	1.151	0.958	1.188	0.871	0.877	0.778	1.175	0.847	0.985	0.856
$^{d}_{8}$-naphthalene	108	1.181	1.163	1.175	1.174	1.066	1.112	1.179	1.206	1.164	1.152
$^{13}C_{6}$-pentachloro-phenol	270	0.264	0.231	0.372	0.259	0.304	0.275	0.449	0.292	0.316	0.255
	272	0.443	0.399	0.589	0.436	0.480	0.455	0.687	0.471	0.506	0.437
toluene	51	0.911	0.997	0.917	0.873	0.894	0.892	0.832	0.881	0.833	0.848
	65	1.309	1.333	1.356	1.396	1.237	1.368	1.343	1.397	1.279	1.382
	91	7.187	7.454	7.430	7.404	6.551	7.201	7.725	7.634	6.969	7.425
chlorobenzene	51	1.877	1.962	1.846	2.040	1.678	1.999	1.798	2.035	1.726	1.834
	112	4.432	4.623	4.480	4.392	3.965	4.327	4.906	4.680	4.410	4.559
	114	1.389	1.437	1.407	1.389	1.256	1.353	1.556	1.488	1.391	1.422
1,1,2,2-tetra-chloroethane	83	4.404	4.618	4.447	4.603	3.987	4.458	4.572	4.752	4.429	4.437
	131	0.322	0.323	0.325	0.342	0.290	0.310	0.362	0.351	0.338	0.332
	168	0.207	0.200	0.203	0.191	0.176	0.195	0.278	0.219	0.208	0.225

(continued)

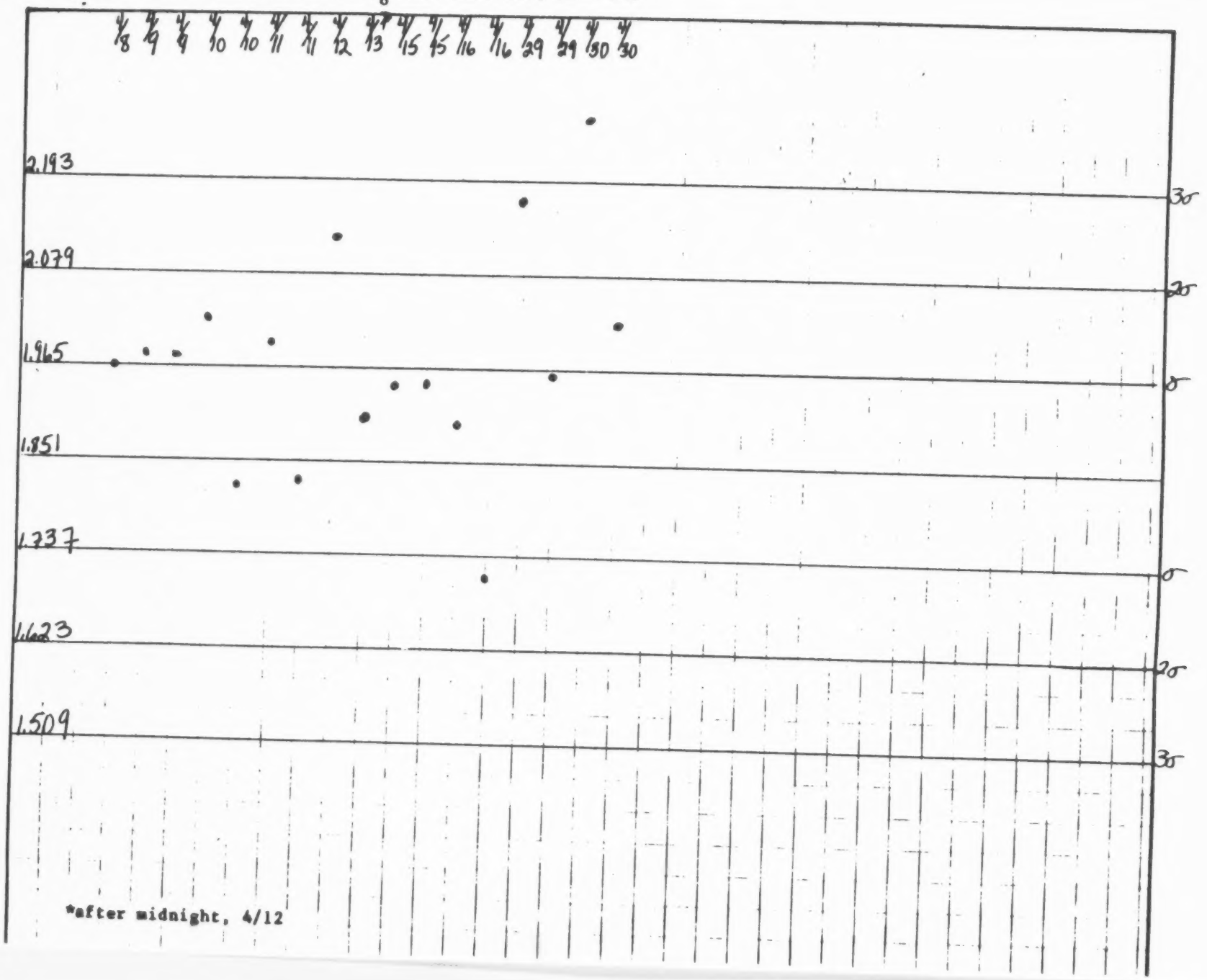
TABLE G-3. (continued)

Compound	Ion	4/15	4/16	4/16	4/29	4/29	4/30	4/30	Mean	SD	%CV	Database Mean	RPD
$^{d}_{10}$-phenanthrene	160	150393	146728	127148	98063	74703	76713	74490	123312	27216	22.1		
$^{d}_{8}$-1,4-dioxane	62	0.491	0.521	0.418	0.542	0.465	0.524	0.460	0.475	0.049	10.4	0.472	0.6
	96	1.484	1.780	1.411	1.490	1.168	1.322	1.233	1.390	0.159	11.4	1.359	2.3
$^{d}_{5}$-pyridine	52	1.220	1.106	1.031	1.439	1.365	1.391	1.366	1.268	0.123	9.7	1.426	11.1
$^{d}_{8}$-toluene	54	0.916	0.930	0.843	1.011	0.892	1.048	0.968	0.941	0.061	6.5	0.899	4.7
	70	1.045	1.150	0.982	1.139	0.977	1.117	1.013	1.067	0.062	5.8	1.025	4.1
$^{d}_{5}$-chlorobenzene	54	1.944	1.894	1.712	2.181	1.959	2.277	2.015	1.973	0.134	6.8	1.851	6.6
	117	4.934	5.361	4.582	4.523	3.847	4.198	3.998	4.573	0.386	8.4	4.345	5.2
	119	1.604	1.723	1.468	1.463	1.229	1.353	1.277	1.472	0.127	8.6	1.374	7.1
$^{d}_{5}$-phenol	71	1.601	1.409	1.469	1.655	1.533	1.646	1.628	1.630	0.137	8.4	1.819	10.4
$^{d}_{5}$-nitrobenzene	98	0.356	0.315	0.359	0.420	0.403	0.390	0.419	0.367	0.045	12.3	0.409	10.3
	128	1.082	1.094	1.030	1.081	0.936	0.860	1.017	0.987	0.128	12.9	1.102	10.4
$^{d}_{8}$-naphthalene	108	1.202	1.041	1.066	1.222	1.154	1.199	1.126	1.152	0.053	4.6	1.124	2.5
$^{13}C_{6}$-pentachloro-phenol	270	0.345	0.381	0.431	0.280	0.291	0.261	0.281	0.311	0.063	20.4	0.311	0
	272	0.583	0.639	0.694	0.473	0.474	0.418	0.463	0.509	0.093	18.4	0.499	2.0
toluene	51	0.838	0.894	0.883	0.942	0.827	0.960	0.809	0.884	0.051	5.8	0.858	3.0
	65	1.322	1.462	1.204	1.445	1.250	1.450	1.261	1.341	0.077	5.8	1.279	4.8
	91	7.468	8.236	7.060	7.483	6.193	6.948	6.401	7.221	0.506	7.0	7.012	3.0
chlorobenzene	51	1.718	1.773	1.577	1.994	1.803	2.081	1.806	1.856	0.143	7.7	1.771	4.8
	112	4.743	5.119	4.388	4.431	3.701	4.051	3.847	4.415	0.367	8.3	4.229	4.4
	114	1.477	1.620	1.378	1.412	1.194	1.315	1.221	1.394	0.110	7.9	1.329	4.9
1,1,2,2-tetra-chloroethane	83	4.707	4.720	4.172	4.248	3.616	4.229	3.709	4.359	0.334	7.7	4.247	2.6
	131	0.362	0.363	0.315	0.322	0.282	0.298	0.296	0.325	0.025	7.8	0.310	4.8
	168	0.236	0.275	0.213	0.200	0.173	0.180	0.179	0.209	0.031	14.8	0.199	5.0

RESPONSE FACTOR CONTROL CHARTS

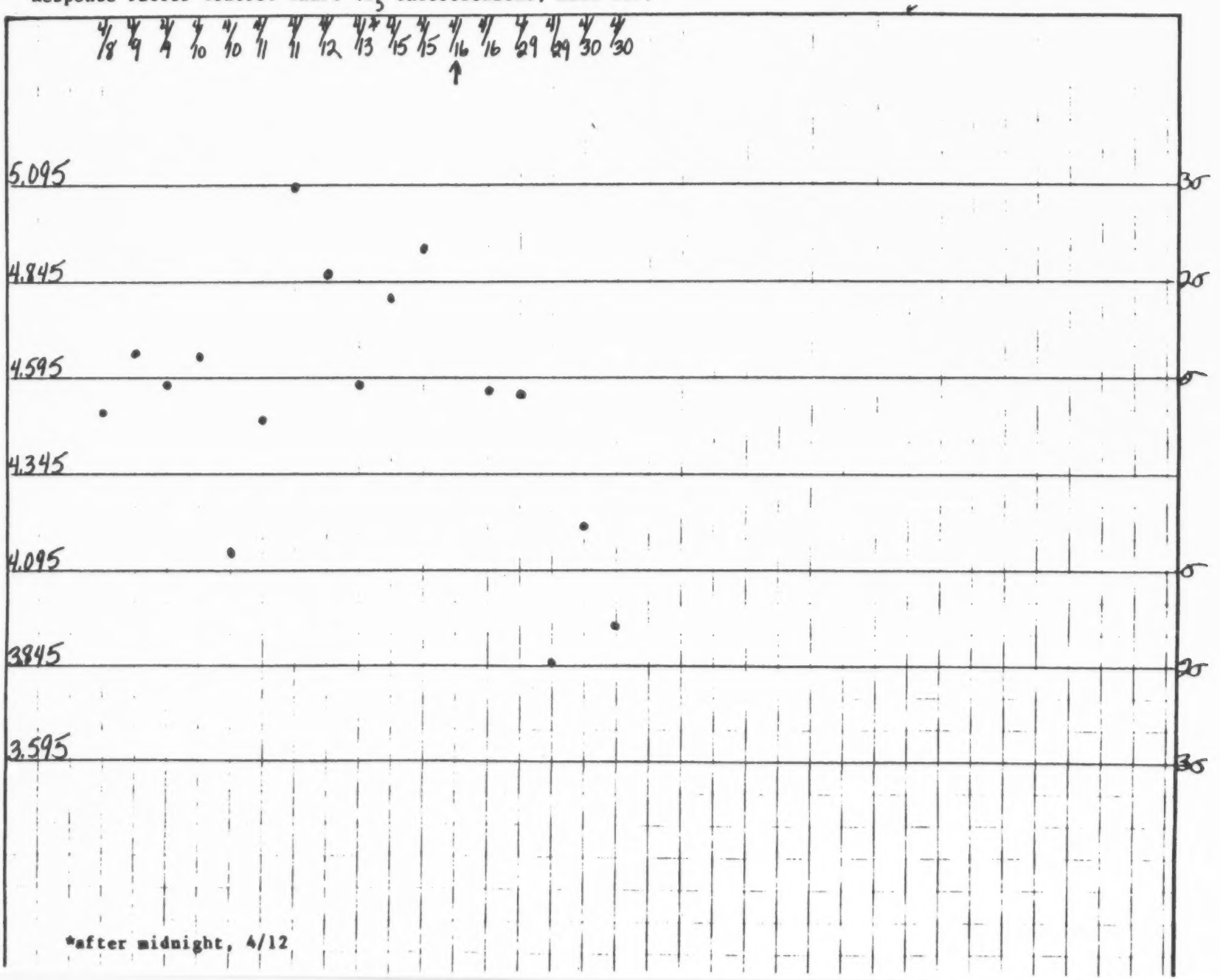
(Example for d_8-Chlorobenzene)

Response Factor Control Chart (d_8-chlorobenzene, mass 54)



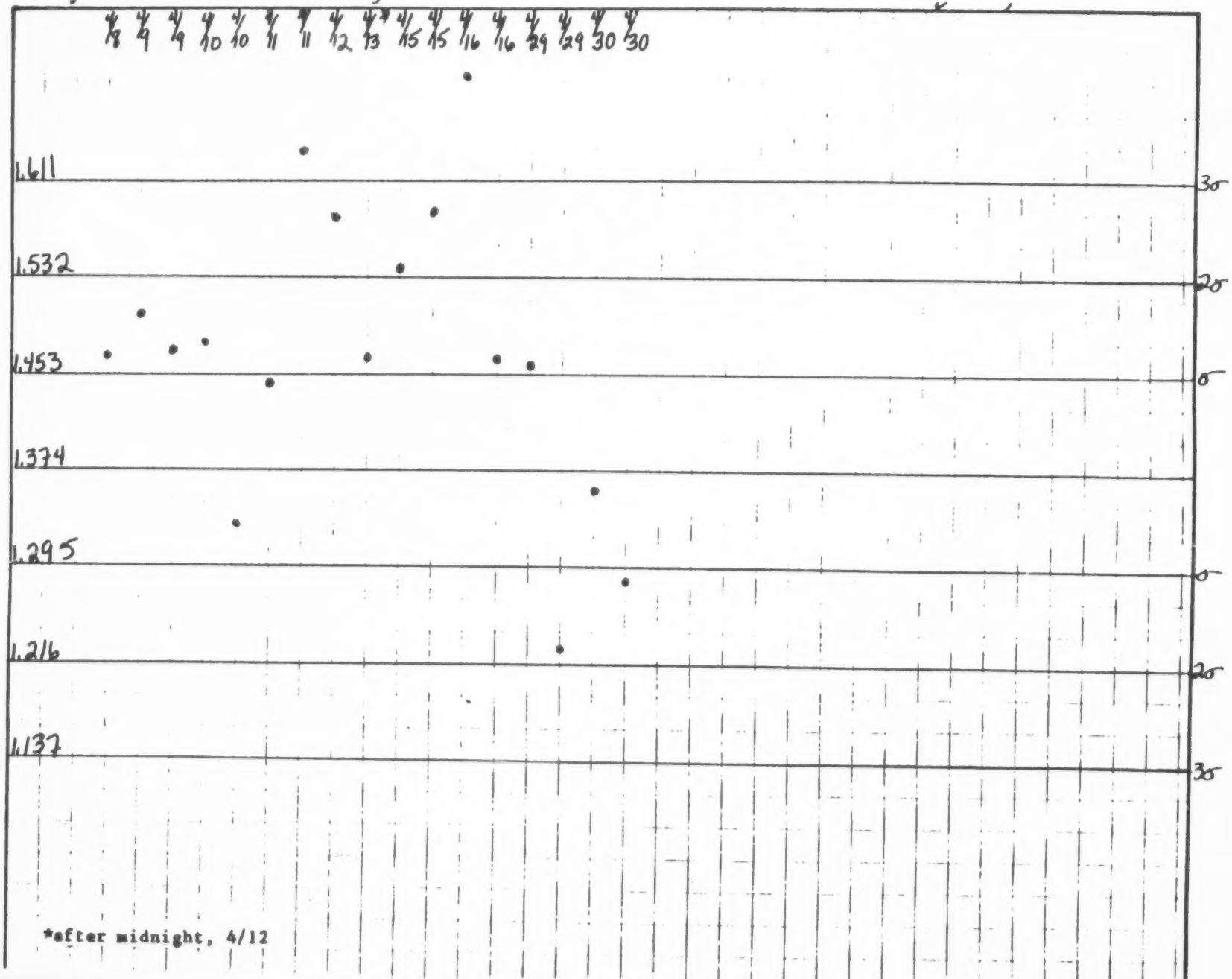
*after midnight, 4/12

Response Factor Control Chart (d_5-chlorobenzene, mass 117)



*after midnight, 4/12

Response Factor Control Chart (d_5-chlorobenzene, mass 119)



*after midnight, 4/12

DAILY TUNING DATA

(Examples)

RADIAN CORPORATION

GC/MS PERFORMANCE STANDARD

Decafluorotriphenylphosphine

INSTRUMENT ID 5100 DATE 4/1/85 TIME 15:17

FRN 5AAA262 QC REPORT NO. 1 ANALYST RP

TUNE CHECK:

m/e	Ion Abundance Criteria	% Relative Abundance
51	30 - 60% of mass 198	50.4
68	less than 2% of mass 69	— ( )[1]
69	mass 69 relative abundance	52.4
70	less than 2% of mass 69	— ( )[1]
127	40 - 60% of mass 198	44.5
197	less than 1% of mass 198	—
198	base peak, 100% relative abundance	100.0
199	5 - 9% of mass 198	6.4
275	10 - 30% of mass 198	17.3
365	greater than 1% of mass 198	1.1
441	less than mass 443	7.6
442	greater than 40% of mass 198	57.2
443	17 - 23% of mass 442	10.5 (18.4)[2]

[1]Value in parenthesis is % mass 69.
[2]Value in parenthesis is % mass 442.

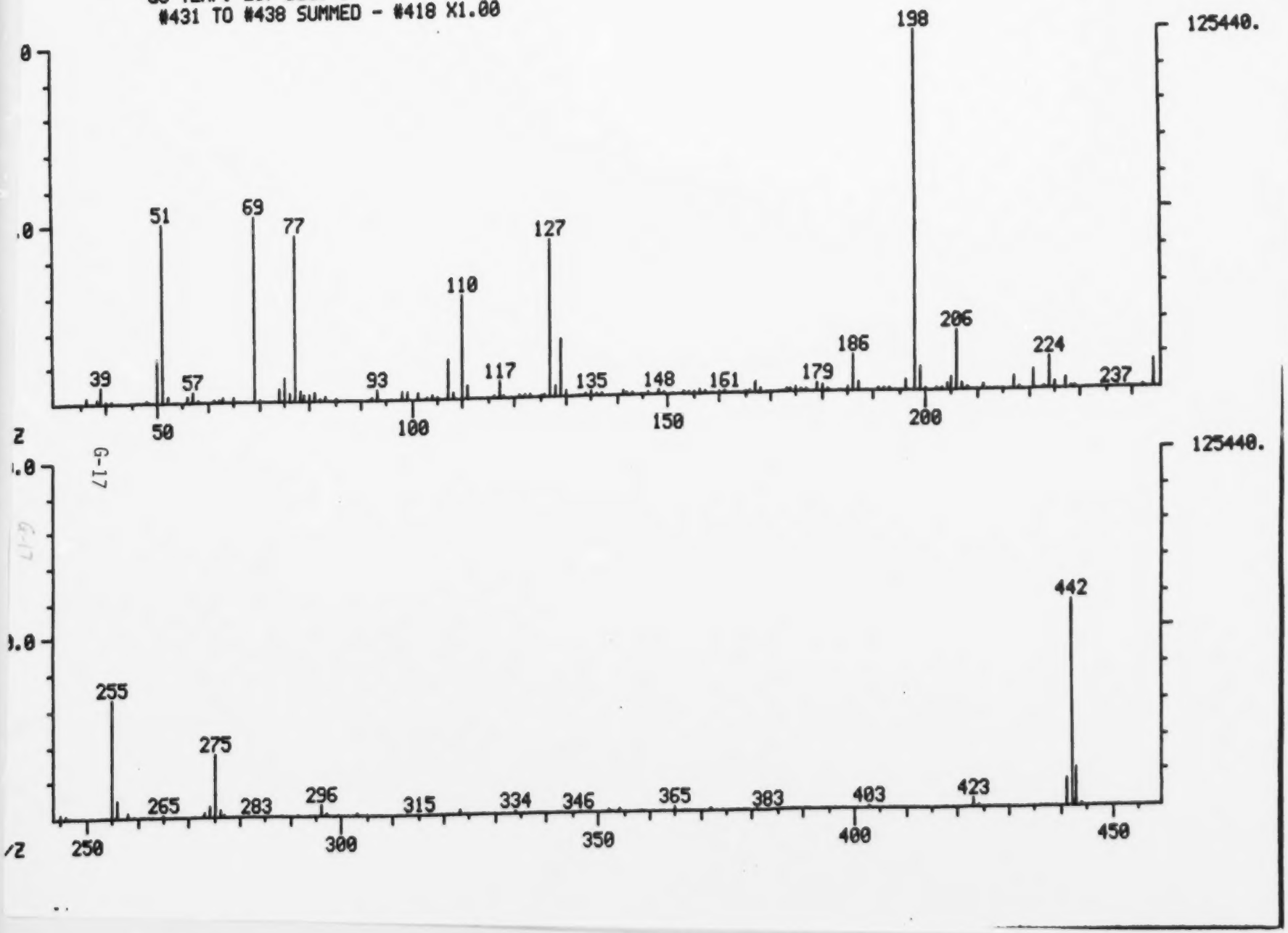
Comments:

QC Form 8409

MASS SPECTRUM
04/01/85 15:17:00 + 7:14
SAMPLE: DFTPP 50 NG
CONDS.: EI
GC TEMP: 257 DEG. C
#431 TO #438 SUMMED - #418 X1.00

DATA: 5AAA262 #1
CALI: 5AAA262 #2

RIC: 886784.



G-17

Project No. _____
Book No. _____
TITLE 5AAA262 DFTPP 50 ng

Mass List
04/01/85 15:17:00 + 7:14 Data: 5AAA262 # 434 Base m/z: 198
Sample: DFTPP 50 NG Cali: 5AAA262 # 2 RIC: 886784.
Conds.: EI
#431 to #438 Summed - #418 X1.00

36 0.00 0.00 0. Minima Min inten: 658.
445 # 0 Maxima

Mass		% RA	% RIC	Inten.	Mass		% RA	% RIC	Inten.
36.00?	S	2.09	0.30	2620.	161.00	S	0.90	0.13	1124.
38.00?	S	1.43	0.20	1790.	167.00		3.22	0.46	4036.
39.00?	S	4.50	0.64	5640.	168.00		1.26	0.18	1578.
50.00?	S	12.47	1.76	15648.	174.00	S	0.59	0.08	736.
51.00?	S	50.41	7.13	63232.	175.00		1.20	0.17	1502.
52.00?	S	2.06	0.29	2580.	176.00		0.78	0.11	974.
56.00?	S	1.52	0.21	1904.	177.00		0.70	0.10	881.
57.00?	S	2.82	0.40	3536.	179.00		2.24	0.32	2812.
61.00?		0.56	0.08	706.	180.00		1.60	0.23	2004.
63.00?	S	1.31	0.19	1644.	181.00		0.73	0.10	911.
65.00?	S	1.07	0.15	1344.	185.00	S	1.05	0.15	1322.
69.00	S	52.35	7.40	65664.	186.00		10.01	1.42	12560.
74.00	S	3.56	0.50	4464.	187.00	S	2.61	0.37	3272.
75.00	S	6.63	0.94	8320.	192.00		0.68	0.10	854.
76.00		2.26	0.32	2832.	193.00		0.78	0.11	980.
77.00	S	46.68	6.60	58560.	196.00		2.83	0.40	3544.
78.00	S	3.08	0.44	3864.	198.00		100.00	14.15	125440.
79.00	S	2.04	0.29	2564.	199.00		6.44	0.91	8080.
80.00		2.01	0.28	2524.	204.00		1.97	0.28	2476.
81.00	S	2.47	0.35	3104.	205.00		3.64	0.52	4568.
82.00	S	0.71	0.10	892.	206.00		16.91	2.39	21216.
83.00	S	1.14	0.16	1436.	207.00	S	1.96	0.28	2456.
85.00	S	0.77	0.11	968.	211.00		0.97	0.14	1220.
92.00	S	0.61	0.09	764.	217.00		3.55	0.50	4448.
93.00	S	3.02	0.43	3792.	221.00	S	5.48	0.77	6872.
98.00	S	2.31	0.33	2892.	223.00		0.77	0.11	967.
99.00		2.34	0.33	2940.	224.00		8.81	1.25	11056.
101.00		1.65	0.23	2076.	225.00		2.08	0.29	2604.
104.00		0.93	0.13	1172.	227.00		2.76	0.39	3468.
105.00	S	0.68	0.10	852.	229.00		0.53	0.07	665.
107.00	S	11.33	1.60	14208.	244.00		7.66	1.09	9632.
108.00		1.82	0.26	2284.	245.00		1.15	0.16	1446.
110.00	S	29.08	4.11	36480.	255.00		32.86	4.65	41216.
111.00	S	3.88	0.55	4864.	256.00		4.92	0.70	6176.
117.00	S	4.83	0.68	6064.	258.00		1.19	0.17	1492.
121.00		0.57	0.08	720.	273.00		0.96	0.14	1202.
123.00	S	0.76	0.11	956.	274.00		3.11	0.44	3896.
125.00		0.62	0.09	779.	275.00		17.30	2.45	21696.
127.00	S	44.49	6.29	55808.	276.00		2.00	0.28	2508.
128.00	S	3.00	0.42	3760.	277.00		0.85	0.12	1060.
129.00	S	16.45	2.33	20640.	296.00		2.93	0.41	3680.
130.00	S	1.73	0.24	2172.	323.00		1.32	0.19	1660.
135.00	S	1.32	0.19	1656.	334.00		0.65	0.09	812.
137.00	S	0.65	0.09	818.	365.00		1.09	0.15	1368.
141.00		1.43	0.20	1796.	372.00		0.58	0.08	732.
142.00		0.62	0.09	775.	423.00		2.51	0.35	3144.
148.00		1.48	0.21	1852.	441.00		7.60	1.08	9536.
153.00		0.55	0.08	690.	442.00		57.24	8.10	71808.
155.00		0.82	0.12	1026.	443.00		10.48	1.48	13152.
156.00		1.45	0.21	1824.	444.00		0.81	0.11	1019.

No.

essed & Understood by me. Date

Date

RADIAN

GC/MS PERFORMANCE STANDARD

Decafluorotriphenylphosphine

INSTRUMENT ID 5100 DATE 4/2/85 TIME 9:06

FRN SAAA 265 QC REPORT NO. 2 ANALYST RP

TUNE CHECK:

m/e	Ion Abundance Criteria	% Relative Abundance
51	30 - 60% of mass 198	57.7
68	less than 2% of mass 69	1.5 (2.5)[1]
69	mass 69 relative abundance	60.6
70	less than 2% of mass 69	— ( )[1]
127	40 - 60% of mass 198	47.5
197	less than 1% of mass 198	—
198	base peak, 100% relative abundance	100.0
199	5 - 9% of mass 198	6.9
275	10 - 30% of mass 198	16.2
365	greater than 1% of mass 198	1.02
441	less than mass 443	8.2
442	greater than 40% of mass 198	63.3
443	17 - 23% of mass 442	11.4 (18.0)[2]

[1]Value in parenthesis is % mass 69.
[2]Value in parenthesis is % mass 442.

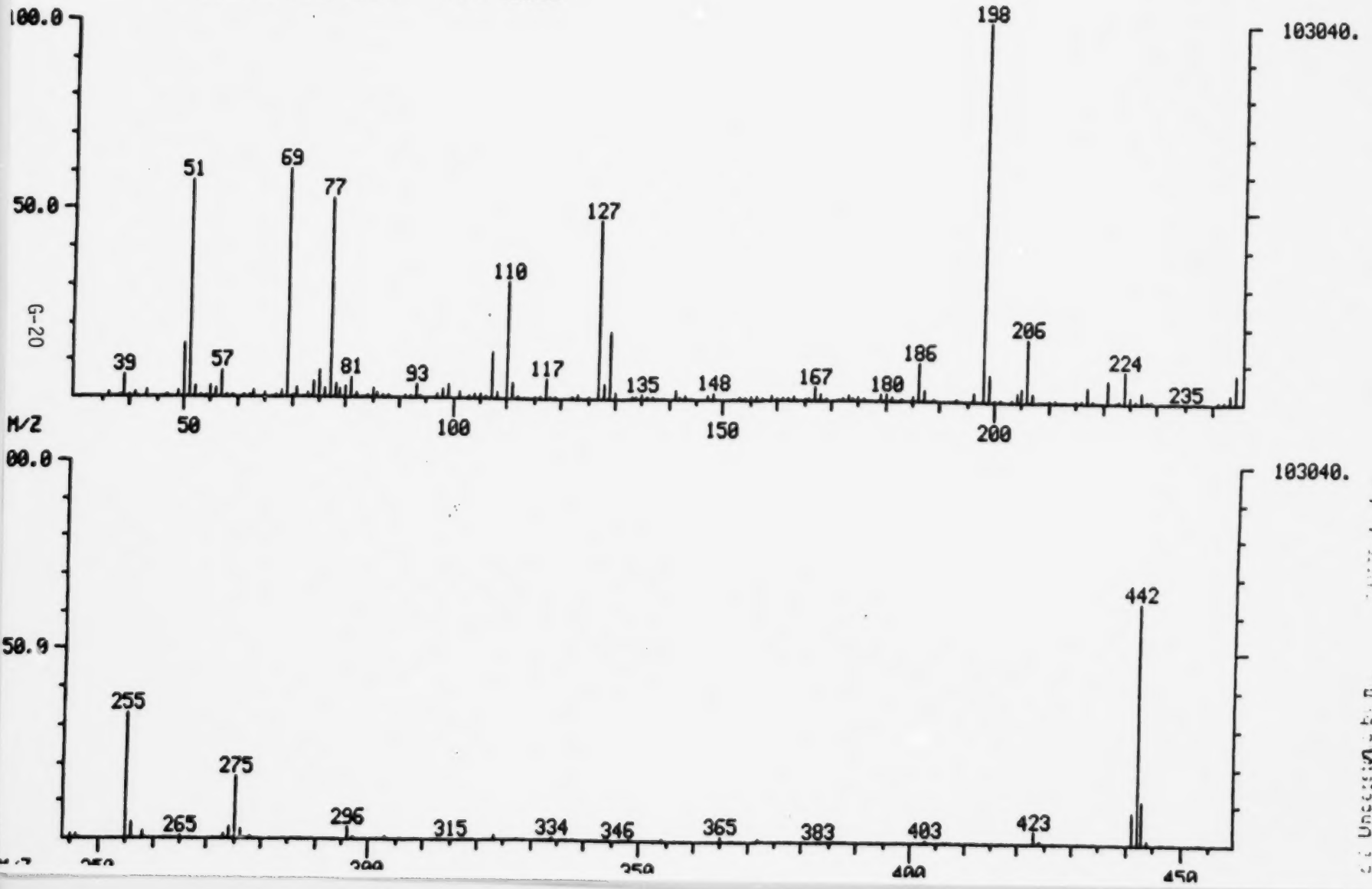
Comments:

QC Form 8409

MID MASS SPECTRUM
04/02/85 9:06:00 + 7:11
SAMPLE: DFTPP
CONDS.: EI
GC TEMP: 256 DEG. C
#442 TO #445 SUMMED - #457 X1.00

DATA: 5AAA265 #443
CALI: 5AAA264 #2

BASE M/Z: 198
RIC: 824320.



G-20

MID Mass List
04/02/85 9:06:00 + 7:11
Sample: DFTPP
Conds.: EI
#442 to #445 Summed - #457 X1.00

Data: 5AAA265 # 443
Cali: 5AAA264 # 2

Base m/z: 198
RIC: 824320.

35 0.00 0.00 0. Minima Min inten: 896.
445 # 0 Maxima

Mass		% RA	% RIC	Inten.	Mass		% RA	% RIC	Inten.
36.00?	S	1.16	0.15	1198.	148.00	S	1.71	0.21	1764.
39.00?	S	5.82	0.73	6000.	155.00	S	0.98	0.12	1012.
41.00?	S	1.30	0.16	1340.	156.00	S	1.46	0.18	1500.
43.00?	S	2.05	0.26	2108.	159.00	S	1.36	0.17	1400.
49.00?	S	1.58	0.20	1628.	161.00	S	0.88	0.11	908.
50.00?	S	14.47	1.81	14912.	163.00	S	0.96	0.12	988.
51.00?	S	57.70	7.21	59456.	165.00	S	0.87	0.11	896.
52.00?	S	2.99	0.37	3084.	167.00	S	3.75	0.47	3864.
53.00?	S	0.89	0.11	912.	168.00	S	2.07	0.26	2132.
55.00?	S	3.04	0.38	3132.	173.00	S	1.45	0.18	1492.
56.00?	S	2.22	0.28	2288.	174.00	S	0.89	0.11	920.
57.00?	S	7.42	0.93	7648.	175.00	S	1.10	0.14	1132.
63.00?	S	1.92	0.24	1976.	179.00	S	1.55	0.19	1592.
65.00?	S	1.09	0.14	1120.	180.00	S	1.72	0.21	1768.
68.00?	S	1.50	0.19	1544.	181.00	S	1.12	0.14	1152.
69.00	S	60.62	7.58	62464.	185.00	S	1.24	0.16	1280.
71.00	S	2.53	0.32	2608.	186.00	S	10.30	1.29	10608.
73.00	S	1.32	0.16	1356.	187.00	S	3.06	0.38	3156.
74.00	S	3.96	0.49	4076.	196.00	S	2.52	0.31	2596.
75.00	S	7.45	0.93	7680.	198.00	S	100.00	12.50	103040.
76.00	S	2.58	0.32	2660.	199.00	S	6.92	0.86	7128.
77.00	S	52.55	6.57	54144.	204.00	S	2.19	0.27	2256.
78.00	S	3.35	0.42	3452.	205.00	S	3.64	0.45	3748.
79.00	S	2.39	0.30	2464.	206.00	S	17.05	2.13	17568.
80.00	S	2.81	0.35	2892.	207.00	S	2.11	0.26	2172.
81.00	S	5.31	0.66	5472.	217.00	S	3.95	0.49	4072.
82.00	S	1.16	0.15	1200.	221.00	S	5.75	0.72	5920.
85.00	S	2.34	0.29	2416.	224.00	S	8.66	1.08	8928.
86.00	S	1.35	0.17	1390.	225.00	S	2.03	0.25	2088.
93.00	S	3.59	0.45	3696.	227.00	S	2.79	0.35	2876.
97.00	S	1.09	0.14	1118.	229.00	S	0.88	0.11	904.
98.00	S	2.36	0.30	2436.	243.00	S	2.48	0.31	2560.
99.00	S	3.63	0.45	3740.	244.00	S	7.86	0.98	8104.
101.00	S	1.71	0.21	1766.	245.00	S	1.37	0.17	1416.
104.00	S	0.93	0.12	962.	246.00	S	1.13	0.14	1164.
105.00	S	1.23	0.15	1264.	255.00		33.17	4.15	34176.
107.00	S	12.59	1.57	12976.	256.00	S	4.19	0.52	4320.
108.00	S	1.66	0.21	1712.	258.00	S	1.89	0.24	1944.
110.00	S	30.93	3.87	31872.	273.00		0.97	0.12	999.
111.00	S	4.49	0.56	4624.	274.00	S	2.92	0.36	3008.
117.00	S	5.28	0.66	5440.	275.00	S	16.21	2.03	16704.
123.00	S	1.04	0.13	1072.	276.00	S	2.17	0.27	2232.
127.00	S	47.52	5.94	48960.	296.00		2.96	0.37	3048.
128.00	S	4.29	0.54	4424.	323.00		1.25	0.16	1292.
129.00	S	18.07	2.26	18624.	365.00		1.02	0.13	1046.
130.00	S	1.60	0.20	1648.	423.00		3.15	0.39	3244.
135.00	S	0.91	0.11	936.	441.00		8.21	1.03	8464.
141.00	S	2.20	0.28	2272.	442.00	S	63.29	7.91	65216.
143.00	S	1.40	0.18	1444.	443.00		11.38	1.42	11728.
[illegible]		[illegible]	[illegible]	[illegible]	444.00		0.96	0.12	994.

RADIAN

GC/MS PERFORMANCE STANDARD

Decafluorotriphenylphosphine

INSTRUMENT ID 5100 DATE 4/3/85 TIME 10:21

FRN 5AAA273 QC REPORT NO. 3 ANALYST RP

TUNE CHECK:

m/e	Ion Abundance Criteria	% Relative Abundance
51	30 - 60% of mass 198	57.1
68	less than 2% of mass 69	— ( )[1]
69	mass 69 relative abundance	60.5
70	less than 2% of mass 69	0.9 (1.5)[1]
127	40 - 60% of mass 198	40.2
197	less than 1% of mass 198	—
198	base peak, 100% relative abundance	100.0
199	5 - 9% of mass 198	6.7
275	10 - 30% of mass 198	14.6
365	greater than 1% of mass 198	1.1
441	less than mass 443	6.7
442	greater than 40% of mass 198	49.9
443	17 - 23% of mass 442	10.1 (20.2)[2]

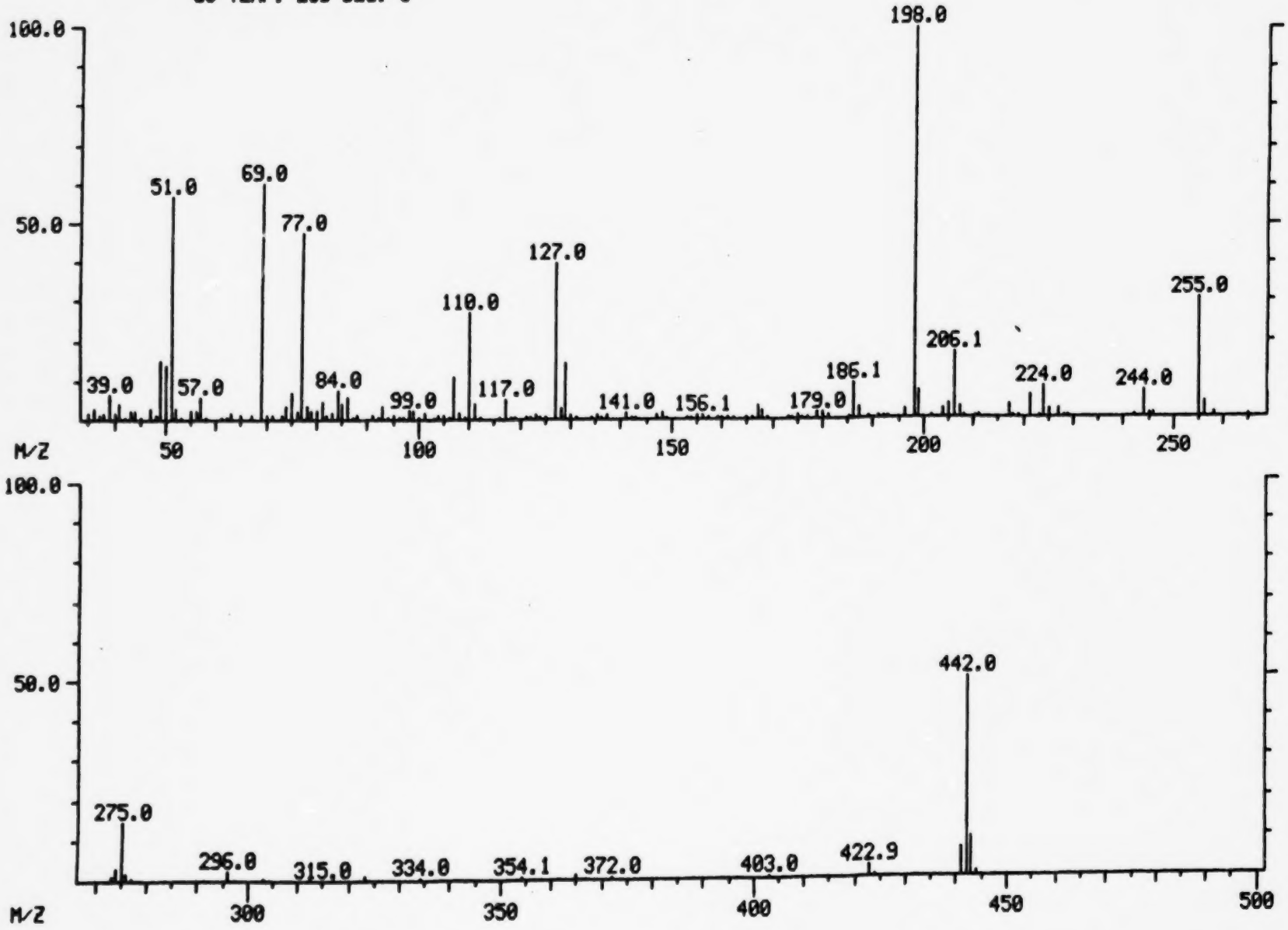
[1]Value in parenthesis is % mass 69.
[2]Value in parenthesis is % mass 442.

Comments:

MID MASS SPECTRUM
04/03/85 10:21:00 + 6:00
SAMPLE: DFTPP
CONDS.: EI
GC TEMP: 259 DEG. C

DATA: 5AAA273 #370
CALI: 5AAA273 #2

BASE M/Z: 198
RIC: 411136.



G-23

Project No.

MID Mass List
04/03/85 10:21:00 + 6:00
Sample: DFTPP
Conds.: EI

Data: 5AAA273 # 370
Cali: 5AAA273 # 2

Base m/z: 198
RIC: 411136.

35 0.00 0.00 0. Minima Min inten: 463.
444 # 0 Maxima

Mass	% RA	% RIC	Inten.	Mass	% RA	% RIC	Inten.
35.01?F	1.74	0.22	921.	117.02 F	5.04	0.65	2672.
36.03?F	2.66	0.34	1410.	123.08 F	1.04	0.13	550.
36.96?	0.93	0.12	495.	127.04 F	40.16	5.18	21280.
38.04?F	1.83	0.24	971.	128.03 F	2.95	0.38	1564.
39.05?F	6.27	0.81	3320.	129.02 F	14.60	1.88	7736.
40.02?F	1.56	0.20	827.	130.05	1.05	0.14	558.
41.07?F	4.10	0.53	2172.	135.06	1.36	0.17	719.
43.08?F	2.57	0.33	1360.	137.14 F	0.93	0.12	494.
44.02?F	2.47	0.32	1310.	141.02	1.45	0.19	771.
47.02?	3.01	0.39	1594.	147.06 F	1.09	0.14	580.
48.01?F	1.30	0.17	691.	148.02	1.51	0.19	798.
49.01?F	15.14	1.95	8024.	155.05	0.89	0.11	470.
50.05?F	13.74	1.77	7280.	156.06	1.44	0.19	765.
51.04?F	57.13	7.36	30272.	167.08 F	3.45	0.44	1826.
52.04?F	2.67	0.34	1416.	168.02 F	2.14	0.28	1136.
55.05?F	2.22	0.29	1174.	175.09	1.17	0.15	621.
56.04?F	2.16	0.28	1146.	179.03 F	1.99	0.26	1056.
57.04?F	5.98	0.77	3168.	180.03 F	1.47	0.19	780.
63.02?	1.91	0.25	1012.	181.06	0.88	0.11	468.
65.05?	1.22	0.16	646.	186.06 F	9.53	1.23	5048.
67.05?F	0.97	0.12	512.	187.05 F	2.68	0.34	1418.
68.96 F	60.51	7.80	32064.	196.11 F	2.59	0.33	1374.
70.07 F	0.93	0.12	492.	198.00 F	100.00	12.89	52992.
71.07	1.18	0.15	627.	199.00 F	6.70	0.86	3548.
73.09 F	0.92	0.12	490.	204.05	2.15	0.28	1138.
74.03 F	3.54	0.46	1878.	205.05 F	3.55	0.46	1882.
75.03 F	6.79	0.87	3596.	206.06 F	16.91	2.18	8960.
76.06 F	2.26	0.29	1200.	207.06 F	3.01	0.39	1594.
77.05 F	47.71	6.15	25280.	216.98 F	3.23	0.42	1714.
78.07 F	3.22	0.42	1708.	221.14 F	6.05	0.78	3204.
79.03 F	2.16	0.28	1146.	224.05 F	8.02	1.03	4248.
80.03 F	2.08	0.27	1104.	225.05 F	2.26	0.29	1198.
81.05 F	4.43	0.57	2348.	226.94	2.57	0.33	1362.
82.04 F	1.29	0.17	682.	244.05 F	7.08	0.91	3752.
83.04 F	2.03	0.26	1076.	245.05	0.89	0.12	474.
83.98 F	7.79	1.00	4128.	246.03 F	0.96	0.12	508.
85.03 F	3.93	0.51	2084.	255.02 F	30.56	3.94	16192.
85.97 F	5.78	0.75	3064.	256.00 F	4.15	0.54	2200.
88.01	1.01	0.13	535.	258.00 F	1.30	0.17	690.
91.04 F	0.89	0.12	473.	273.00	0.92	0.12	487.
93.02 F	3.70	0.48	1960.	274.03 F	2.75	0.35	1458.
95.12 F	1.02	0.13	543.	275.03 F	14.64	1.89	7760.
98.04 F	2.17	0.28	1150.	276.03 F	1.92	0.25	1020.
99.02 F	2.51	0.32	1328.	296.00	2.40	0.31	1274.
101.02	1.62	0.21	859.	323.06	1.11	0.14	587.
104.03 F	0.92	0.12	489.	364.97	1.10	0.14	584.
105.03 F	1.01	0.13	536.	422.91 F	2.84	0.37	1506.
107.03 F	11.11	1.43	5888.	441.00 F	6.73	0.87	3564.
108.03	1.64	0.21	871.	442.00 F	49.88	6.43	26432.
110.03 F	27.05	3.49	14336.	443.00 F	10.14	1.31	5376.
111.05	4.02	0.52	2128	444.00 F	0.93	0.12	495.

RADIAN

GC/MS PERFORMANCE STANDARD

Decafluorotriphenylphosphine

INSTRUMENT ID 5100 DATE 4/4/85 TIME 9:03

FRN SAAA277 QC REPORT NO. 4 ANALYST RP

TUNE CHECK:

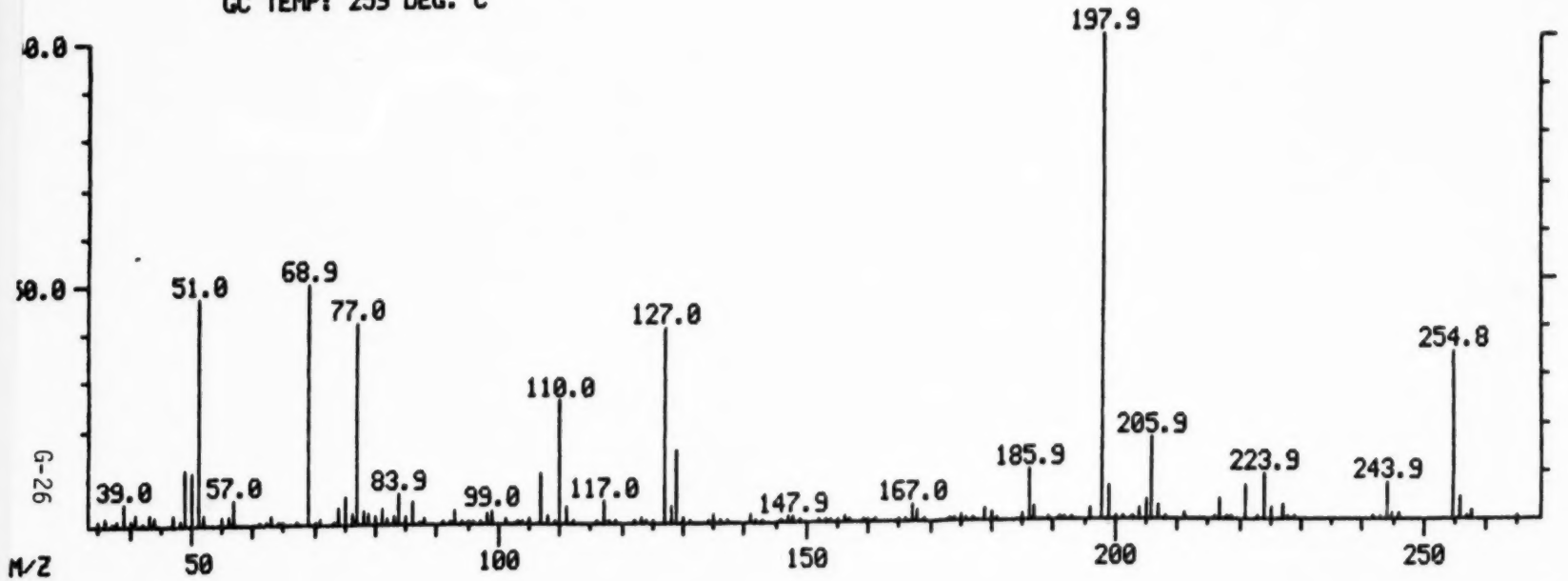
m/e	Ion Abundance Criteria	% Relative Abundance
51	30 - 60% of mass 198	47.3
68	less than 2% of mass 69	— ( )[1]
69	mass 69 relative abundance	50.0
70	less than 2% of mass 69	0.8 (1.6)[1]
127	40 - 60% of mass 198	40.5
197	less than 1% of mass 198	—
198	base peak, 100% relative abundance	100.0
199	5 - 9% of mass 198	6.8
275	10 - 30% of mass 198	17.0
365	greater than 1% of mass 198	1.3
441	less than mass 443	9.6
442	greater than 40% of mass 198	71.5
443	17 - 23% of mass 442	13.3 (18.6)[2]

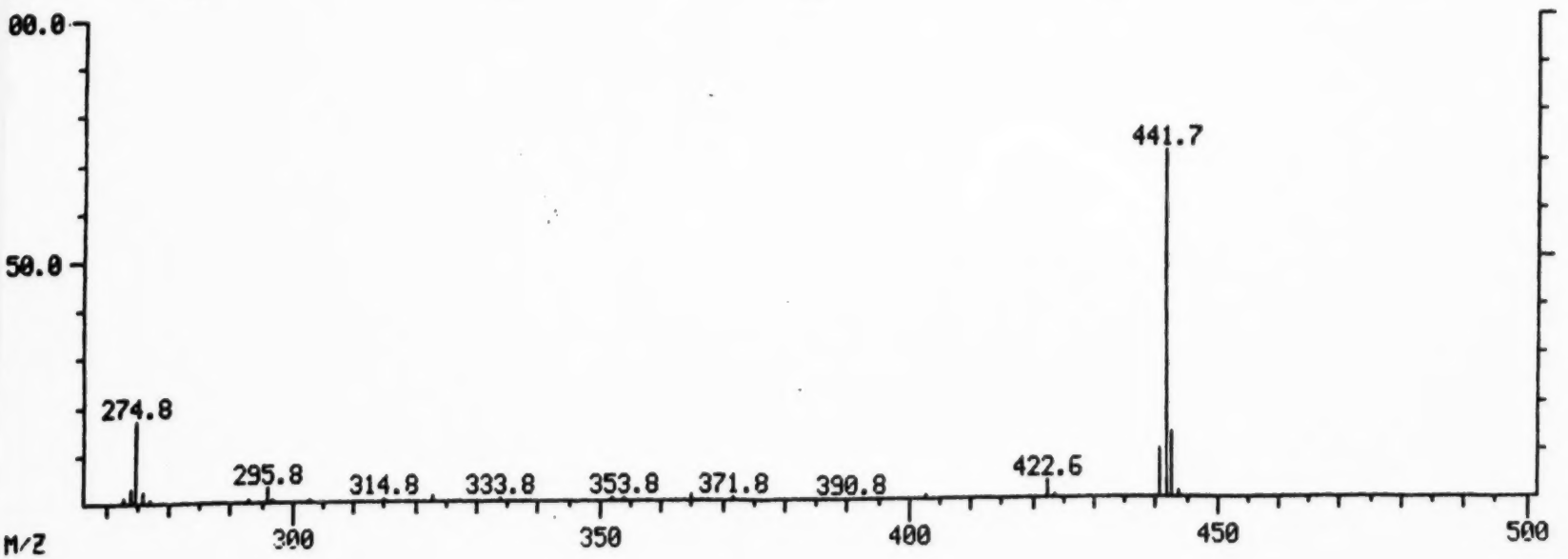
[1]Value in parenthesis is % mass 69.
[2]Value in parenthesis is % mass 442.

Comments:

QC Form 8409

04/04/85 9:03:00 + 5:42
SAMPLE: DFTPP 50NG
CONDS.: EI
GC TEMP: 259 DEG. C





Project No.
Book No.
TITLE
SAMPLE 77

MID Mass List Data: 5AAA277 # 352 Base m/z: 198
04/04/85 9:03:00 + 5:42 Cali: 5AAA277 # 2 RIC: 451584.
Sample: DFTPP 50NG
Conds.: EI

35 0.00 0.00 0. Minima Min inten: 467.
444 # 0 Maxima

Mass	% RA	% RIC	Inten.	Mass	% RA	% RIC	Inten.
35.00?	1.38	0.18	817.	129.92	1.16	0.15	684.
35.98?	1.95	0.25	1150.	134.97	1.52	0.20	897.
38.01?F	1.06	0.14	628.	137.02 F	0.81	0.11	480.
39.02?F	4.60	0.60	2716.	140.94 F	1.50	0.20	889.
39.98?F	1.16	0.15	685.	146.94	0.97	0.13	575.
41.02?F	2.36	0.31	1392.	147.91	1.42	0.19	841.
43.06?F	2.13	0.28	1260.	154.92	0.82	0.11	482.
43.98?F	1.71	0.22	1012.	155.95 F	1.39	0.18	824.
46.97?	2.07	0.27	1222.	160.94	0.82	0.11	483.
48.01?F	1.08	0.14	639.	166.95 F	3.35	0.44	1978.
48.98?F	11.82	1.55	6984.	167.94 F	2.14	0.28	1266.
50.01?F	10.89	1.42	6432.	174.95 F	1.17	0.15	692.
51.02?F	47.29	6.19	27936.	178.89 F	2.36	0.31	1394.
52.02?	2.29	0.30	1350.	179.91 F	1.64	0.21	969.
55.06?F	1.66	0.22	982.	180.94	0.84	0.11	498.
56.00?F	1.86	0.24	1098.	184.92	1.09	0.14	643.
57.01?F	5.17	0.68	3056.	185.94 F	10.37	1.36	6128.
63.00?F	1.64	0.21	967.	186.92 F	2.64	0.35	1562.
65.02?	0.87	0.11	514.	195.95 F	2.59	0.34	1528.
68.92 F	50.00	6.54	29536.	197.86 F	100.00	13.08	59072.
70.02 F	0.83	0.11	489.	198.87 F	6.84	0.89	4040.
71.05	1.00	0.13	589.	203.91 F	2.10	0.28	1242.
74.01 F	3.39	0.44	2004.	204.92 F	3.99	0.52	2356.
74.97 F	5.89	0.77	3480.	205.92 F	16.87	2.21	9968.
76.04 F	2.11	0.28	1248.	206.92	3.05	0.40	1802.
77.01 F	41.60	5.44	24576.	210.95 F	0.95	0.12	562.
78.02 F	2.95	0.39	1744.	216.84 F	3.91	0.51	2308.
78.98 F	2.32	0.30	1372.	220.98 F	6.81	0.89	4020.
79.96 F	1.96	0.26	1156.	222.83 F	0.84	0.11	498.
80.97 F	3.26	0.43	1924.	223.89 F	9.03	1.18	5336.
81.99 F	1.12	0.15	661.	224.89 F	2.22	0.29	1312.
83.03 F	1.52	0.20	897.	226.80	2.87	0.38	1694.
83.92 F	6.52	0.85	3852.	243.87 F	7.71	1.01	4552.
84.99 F	1.51	0.20	894.	244.91 F	1.07	0.14	632.
85.92 F	4.49	0.59	2652.	245.84	0.89	0.12	525.
87.93 F	1.04	0.14	613.	254.84 F	34.62	4.53	20448.
90.97	0.85	0.11	504.	255.84 F	4.74	0.62	2800.
92.95 F	3.18	0.42	1880.	257.81 F	1.47	0.19	866.
97.96 F	2.23	0.29	1320.	272.84 F	0.88	0.11	519.
98.97 F	2.76	0.36	1632.	273.84 F	3.01	0.39	1780.
100.97	1.22	0.16	720.	274.84 F	16.96	2.22	10016.
104.98	1.00	0.13	592.	275.84 F	2.15	0.28	1270.
106.97 F	10.22	1.34	6040.	276.81 F	0.86	0.11	509.
107.98 F	1.71	0.22	1012.	295.78	3.12	0.41	1846.
109.96 F	25.54	3.34	15088.	322.81	1.31	0.17	773.
110.98 F	3.49	0.46	2060.	364.72 F	1.27	0.17	749.
116.95 F	4.77	0.62	2820.	422.62 F	3.45	0.45	2036.
122.98	0.97	0.13	572.	440.69 F	9.62	1.26	5680.
126.95 F	40.52	5.30	23936.	441.69 F	71.51	9.35	42240.
127.95 F	3.21	0.42	1898.	442.72 F	13.26	1.73	7832.
128.92 F	15.36	2.01	9072.	443.72 F	1.07	0.14	633.

Witnessed & Understood by ....